# A general phenomenon of spontaneous amplification of optical purity under an achiral chromatographic conditions

***(ESI)***

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# CHEMISTRY

## GENERAL INFORMATION AND TYPICAL PROCEDURES

All the chemicals used in this research were purchased from Sigma-Aldrich, Avantor Performance Materials Poland S.A. (formerly POCH S.A) and Merck. Analytical thin-layer chromatography (TLC) was performed using silica gel 60 $F_{254}$ precoated plates (0.25 mm thickness). Visualization of TLC plates was performed by means of UV light. NMR spectra were recorded on Bruker Avance 500 MHz spectrometers, and chemical shifts are reported in ppm, and calibrated to residual solvent peaks at 7.27 ppm and 77.00 ppm for $^{1}H$ and $^{13}C$ in $CDCl_3$ or TMS as internal reference compounds. The enantiomeric compositions of the obtained fractions was determined by a chromatographic method (Shimadzu LCMS IT-TOF spectrometer) using chiral chromatographic columns Chiralpak® and Chiralcel® with the following dimensions: 150 x 2.1 mm, or by $^{1}H$ NMR and $^{13}C$ NMR techniques using an appropriate chiral differentiating factor and solvents. The purification process and the study of the SDE phenomenon were conducted on a flash low pressure BUCHI chromatograph using 12x150 mm PE columns packed with 10 g spherical silica gel 60 with the particle size of 230-400 mesh as the stationary phase. The studied compounds were dissolved in 5 mL of an appropriate solvent and mixed with 1g of silica gel. Next, the solvent was evaporated and the sample supported on silica was placed at the top of the column prepacked with 10 g of silica. After that the column was connected to the MPLC to be subjected to SDE studies. In the case of compounds **1** and **6**, instead of supporting them on silica, the solutions of the studied compounds in 0.6 mL of pure hexane were injected onto the column prepacked with 11g of silica and prewashed with the mobile phase. The fractions were automatically collected by 18 mL volume. The elution progress was monitored by TLC.

The double injection experiment (compound **6,** MBTE as an eluent) was carried out as below: in the first case, on the prepared column (the same parameters of the column as previously) the injected compound dissolved in 0.5 mL of pure methyl *tert*-butyl ether and the collected fraction was monitored by the TLC technique. In the next step, when in the collected fraction, the compound was nowhere to be found, the next portion of the same initial mixture was injected and then the fractions from the second injection were collected. The volume of the fractions in both runs equals 18 mL. The obtained fractions were evaporated and dried. In the next step, the fractions were weighed and samples were prepared, using appropriate differentiating agents and solvents. The enantiomeric compositions of the obtained fractions were determined by $^{1}H$ NMR and $^{13}C$ NMR techniques.

## COMPUTATIONAL STUDIES

All DFT calculations were performed using the "Prometheus" cluster in the "Cyfronet" computational centre in Cracow. A new generation M062x [1]; [2] functional, implemented in the Gaussian 09 package [3], was used. This functional has been recently used by us to resolve several similar problems [4]; [5]; [6]. All stationary structures have been optimised using the advanced 6-311++G(d,p) basis set and were characterised by only positive eigenvalues in their diagonalised Hessian matrices. For the optimised structures, thermochemical data for the temperature T = 298 K and pressure p = 1atm were computed using vibrational analysis data. For the simulation of the solvent presence, the PCM model has been applied, similarly as in previous our works [5,6].

# TABLES, SPECTRA, CHROMATOGRAMS

**Table 1-ESI.** SDE and the analysis of the enantiomeric composition of compound **1**.

| Fraction | Elution volume, [mL] | Total amount of 1, [mg] | Ratio of enantiomers* *R-*/*S-*, [mg/mg] | Ee, [%] |
|---|---|---|---|---|
| Eluent: *hexane* / *acetone = 99* / *1* | | | | |
| 1 | 18 | 1.9 | 1.4 / 0.5 | **49.2** |
| 2 | 36 | 6.2 | 4.8 / 1.4 | **49.0** |
| 3 | 54 | 8.7 | 6.5 / 2.2 | **49.5** |
| 4 | 72 | 6.3 | 4.7 / 1.6 | **49.1** |
| 5 | 90 | 7.3 | 5.5 / 1.8 | **50.2** |
| 6 | 108 | 4.2 | 3.1 / 1.0 | **50.1** |
| 7 | 126 | 2.1 | 1.6 / 0.5 | **51.0** |
| Total amount: | | 36.6 | 27.6 / 9 | |
| Eluent: *hexane* / *acetone = 99.7* / *0.3* | | | | |
| 1 | 18 | 2.1 | 1.5 / 0.6 | **47.0** |
| 2 | 36 | 8.3 | 6.2 / 2.1 | **49.5** |
| 3 | 54 | 12.4 | 9.3 / 3.1 | **50.0** |
| 4 | 72 | 6.2 | 4.7 / 1.5 | **50.1** |
| 5 | 90 | 4.1 | 3.1 / 1.0 | **52.2** |
| 6 | 108 | 1.1 | 0.9 / 0.2 | **54.0** |
| Total amount: | | 34.3 | 25.7 / 8.5 | |

*Calculated based on ee and total amount

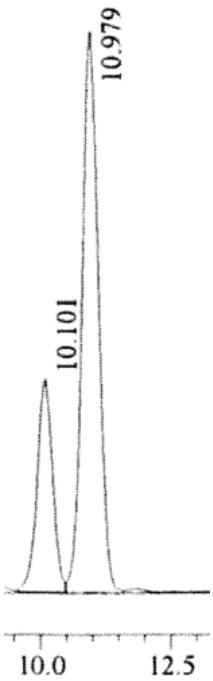


**Figure 1-ESI.** Chiral HPLC chromatogram of the selected fraction of compound **1**. *Chiralpak® AS-RH column and mobile phase $H_2O$ / $CH_3CN$ = 55 / 45, and 0.4 mL/min flow.*

**Table 2-ESI.** SDE of compound **2**.

| Fraction | Elution volume [mL] | Ee, [%] |
|---|---|---|
| 32 | 576 | 21.0 |
| 34 | 594 | 28.0 |
| 36 | 612 | 31.0 |
| 38 | 630 | 36.0 |
| 40 | 648 | 42.0 |
| 42 | 666 | 48.0 |
| 46 | 684 | 55.0 |
| 48 | 702 | 58.0 |
| 50 | 720 | 59.0 |
| 52 | 738 | 63.0 |
| 32 | 756 | 21.0 |
| 34 | 774 | 28.0 |

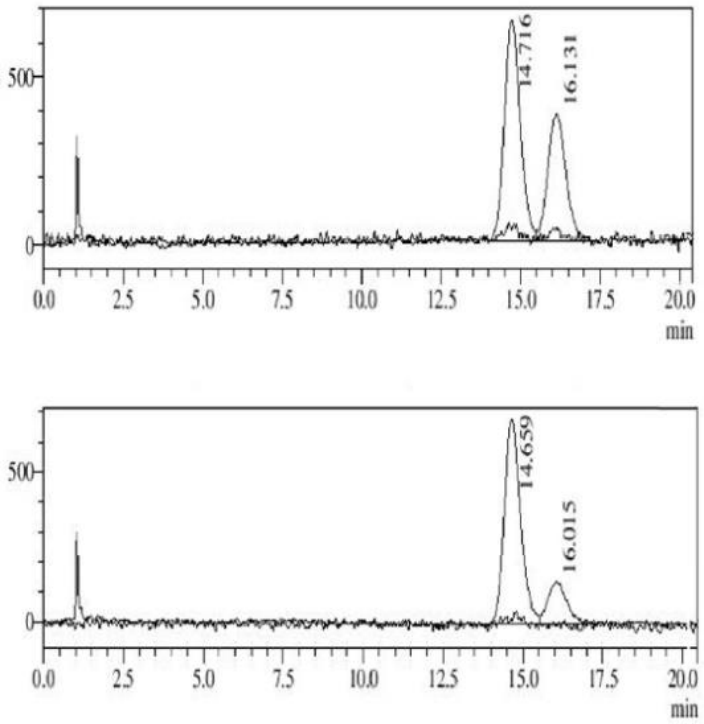


**Figure 2-ESI.** Chiral HPLC chromatograms of selected fractions of compound **2**.
*CHIRALPAK® AS-RH column, and the mobile phase $H_2O$ / $CH_3CN$ = 50 / 50, and 0.3 mL/min flow.*

**Table 3-ESI.** SDE of compound **3** via MPLC on the achiral stationary phase using hexane / $^{t}$butyl methyl ether (85 / 15) as the eluent.

| 50 mg of 3 | | 100 mg of 3 | | 150 mg of 3 | |
|---|---|---|---|---|---|
| **Fraction** | **Ee, [%]** | **Fraction** | **Ee, [%]** | **Fraction** | **Ee, [%]** |
| 37 | **55.6** | 29 | **52.5** | 29 | **48.8** |
| 40 | **52.0** | 33 | **49.5** | 33 | **46.0** |
| 43 | **48.8** | 37 | **47.4** | 37 | **45.2** |
| 46 | **44.6** | 41 | **45.7** | 41 | **43.0** |
| 49 | **41.5** | 45 | **44.6** | 45 | **41.0** |
| 52 | **39.1** | 49 | **43.9** | 49 | **38.9** |
| 55 | **38.0** | 53 | **43.2** | 53 | **37.8** |
| 58 | **36.7** | 57 | **42.2** | 57 | **37.0** |
| 61 | **34.8** | 61 | **41.9** | 61 | **36.2** |
| 64 | **33.2** | 65 | **39.9** | 65 | **35.3** |
| 67 | **35.6** | 69 | **38.4** | 69 | **35.0** |
| 70 | **32.0** | 73 | **37.7** | 71 | **32.0** |
| | | 77 | **36.4** | | |
| | | 81 | **35.9** | | |
| | | 85 | **35.3** | | |

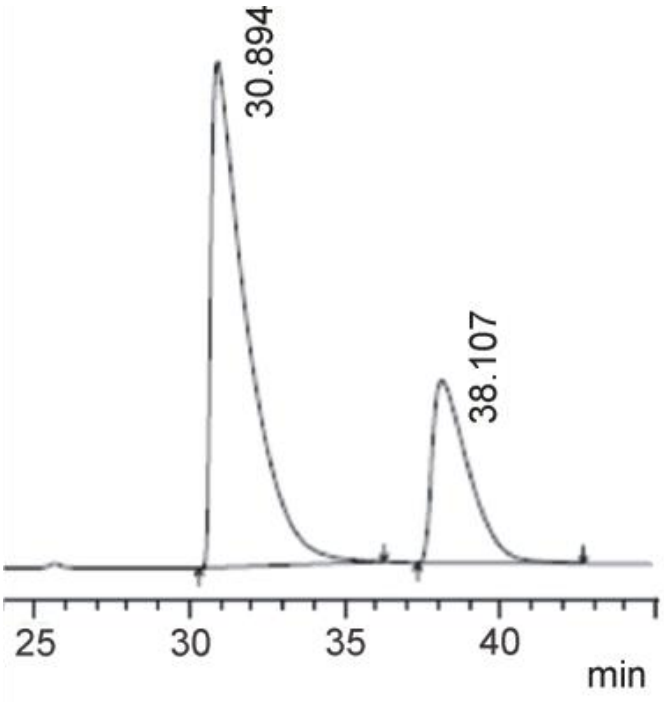


**Figure 3-ESI.** Chiral HPLC chromatogram of selected fraction of compound **3**. *Chiralpak® AD-RH column, and the $CH_3CN$ / $H_2O$ = 30 / 70.*

**Table 4-ESI.** SDE of compound **4**.

| Fraction | Amount, [mg] | Ee, [%] | Fraction | Amount, [mg] | Ee, [%] | Fraction | Amount, [mg] | Ee, [%] |
|---|---|---|---|---|---|---|---|---|
| *Initial ee = 27%* | | | *Initial ee = 60%* | | | *Initial ee = 75%* | | |
| 7 | 12 | **28** | 6 | 5 | **59** | 9 | 11 | **76** |
| 8 | 9 | **28** | ***7*** | 3 | ***60*** | 10 | 15 | **75** |
| 9 | 1 | **28** | 8 | 2 | **60** | 11 | 5 | **75** |
| 10 | 2 | **26** | 9 | 1 | **60** | 12-24 | 33 | **73** |
| 11 | 1 | **27** | 10 | 1 | **59** | | | |
| 12-23 | 39 | **25** | 11 | 5 | **58** | | | |
| | | | 12 | 8 | **56** | | | |
| | | | 13-22 | 21 | **56** | | | |

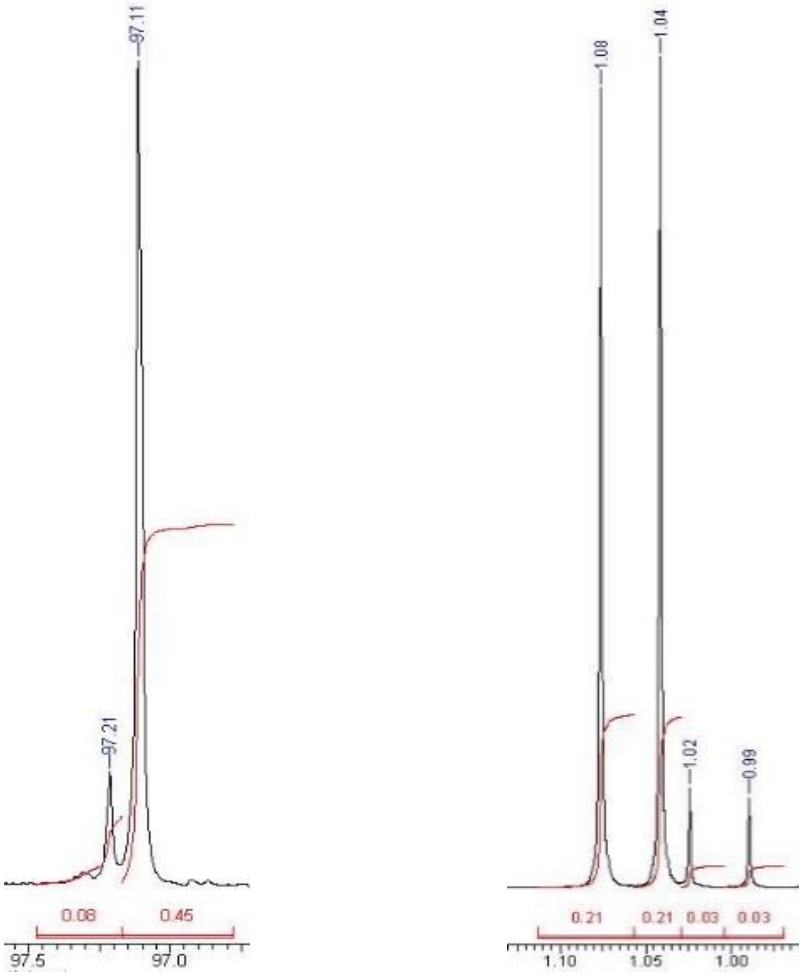


**Figure 4-ESI.** The fragments of the $^{31}P$ and $^{1}H$ NMR spectra of selected fractions of compound **4**.

**Table 5-ESI.** SDE of compound **5**.

| Fraction | Amount of 5, [mg] | Ratio of isomers R/S, [mg/mg]* | Ee, [%] |
|---|---|---|---|
| Eluent: *Hexane / i-PrOH = 92 / 8* | | | |
| 9 | 6.1 | 4.7 / 1.4 | **53.51** |
| 10 | 9.9 | 7.4 / 2. 5 | **49.62** |
| 11 | 13.6 | 6.8 / 2.4 | **47.86** |
| 12 | 9.2 | 6.9 / 2.0 | **48.56** |
| 13 | 4.8 | 3.6 / 1.2 | **50.55** |
| 14 | 4.1 | 3.0 / 1.0 | **48.73** |
| 15 | 3.3 | 2.4 / 0.9 | **46.11** |
| 16 | 2.7 | 2.0 / 0.7 | **46.07** |
| 17 | 2.1 | 1.6 / 0.6 | **45.99** |
| 18 | 2.2 | 1.8 / 0.6 | **49.49** |
| 19 | 2.2 | 1.6 / 0.6 | **44.73** |
| 20 | 1.7 | 1.2 / 0.5 | **45.39** |
| 21 | 1.7 | 0.8 / 0.3 | **46.79** |
| 22 | 1.2 | 0.9 / 0.3 | **47.23** |
| 23 | 1.3 | 1.0/ 0.4 | **47.61** |
| Total amount: | 66.1 | 49.1 / 16.7 | |
| Eluent: *dichloroethane* | | | |
| 12 | 2.0 | 1.4 / 0.6 | **42.80** |
| 13 | 3.7 | 2.7 / 1.0 | **46.53** |
| 14 | 5.6 | 4.1 / 1.5 | **47.81** |
| 15 | 5.7 | 4.2 / 1.5 | **46.85** |
| 16 | 5.9 | 4.3 / 2.0 | **37.41** |
| 17 | 5.6 | 4.0 / 1.6 | **43.41** |
| 18 | 5.4 | 3.8 / 1.6 | **40.64** |
| 19 | 4.6 | 3.3 / 1.3 | **42.98** |
| 20 | 3.9 | 2.8 / 1.0 | **46.24** |
| 21 | 2.8 | 2.1 / 0.7 | **47.51** |
| 22 | 1.8 | 1.3 / 0.4 | **50.34** |
| Total amount: | 47 | 34.0 / 13.0 | |

*Calculated based on ee and total amount

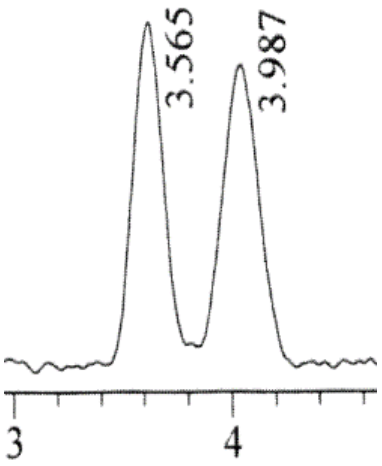


**Figure 5-ESI.** Chiral HPLC chromatogram of selected fraction of compound **5**.
*Chiralpak® OJ-RH, $H_2O$ / $CH_3CN$ = 85 / 15, 0.3 mL/min.*

**Table 6-ESI**. SDE of compound **6** in diethyl ether.

| Fraction | Amount of 6, [mg] | Ratio of isomers R/S, [mg/mg] | Ee, [%] | | | |
|---|---|---|---|---|---|---|
| | | | $^{1}$H NMR | $^{13}$C NMR | $^{13}$C NMR | Average |
| Eluent: *diethyl ether* | | | | | | |
| 12 | 1.5 | 0.5 / 1.0 | 36.9 | 39.8 | 41.8 | **39.5** |
| 13 | 6.0 | 1.7 / 4.3 | 46.5 | 40.5 | 39.9 | **42.3** |
| 14 | 5.8 | 1.8 / 4.0 | 36.5 | 41.4 | 36.1 | **38.0** |
| 15 | 10.6 | 3.3 / 7.3 | 38.3 | 31.5 | 40.8 | **36.9** |
| 16 | 9.1 | 2.8 / 6.3 | 36.3 | 33.9 | 46.0 | **38.7** |
| 17 | 11.4 | 3.5 / 7.9 | 36.1 | 27.9 | 43.9 | **36.0** |
| 18 | 4.7 | 1.6 / 3.1 | 28.8 | 30.2 | 42.9 | **33.9** |
| 19 | 6.3 | 2.0 / 4.3 | 33.3 | 36.3 | 38.9 | **36.0** |
| 20 | 5.2 | 1.8 / 3.4 | 32.2 | 24.6 | 36.1 | **30.9** |
| 21 | 3.8 | 1.4 / 2.4 | 28.8 | 22.8 | 29.9 | **27.2** |
| 22 | 3.7 | 1.4 / 2.3 | 27.3 | 30.0 | 19.8 | **25.7** |
| Total amount: | 68.1 | 21.8 / 46.3 | | | | |

**Table 7-ESI.** SDE of co mpound **6** eluted by *tert*-butyl methyl ether.

| Fraction | Amount of 6, [mg] | Ratio of isomers R/S, [mg/mg] | **Ee, [%]** measured by | | | Average ee, [%] |
|---|---|---|---|---|---|---|
| | | | $^{1}$H NMR | $^{13}$C NMR | $^{13}$C NMR | |
| *1$^{st}$ separation* | | | | | | |
| 7 | 7.5 | 2.2 / 5.3 | 40.9 | 37.0 | 43.6 | **40.5** |
| 8 | 18.7 | 5.7 / 13.0 | 38.9 | 40.9 | 34.5 | **38.1** |
| 9 | 16.5 | 5.2 / 11.3 | 37.0 | 31.6 | 39.0 | **35.9** |
| 10 | 10.5 | 3.5 / 7.0 | 34.2 | 31.6 | 35.0 | **33.6** |
| 11 | 6.6 | 2.2 / 4.4 | 32.5 | 36.1 | 29.8 | **32.8** |
| 12 | 2.9 | 1.0 / 1.9 | 26.6 | 33.3 | 29.1 | **29.7** |
| 13 | 3.3 | 1.2 / 2.1 | 30.7 | 22.0 | 25.8 | **26.3** |
| 14 | 3.0 | 1.1 / 1.9 | 24.2 | 24.2 | 24.6 | **24.2** |
| Total amount: | 68.0 | 22.3 / 46.7 | | | | |
| *2$^{nd}$ separation* | | | | | | |
| 36 | 0.5 | 0.1 / 0.4 | 42.6 | 46. | 39.3 | **42.7** |
| 37 | 7.6 | 2.3 / 5.3 | 41.8 | 41.8 | 38.0 | **40.6** |
| 38 | 24.1 | 7.7 / 16.4 | 38.9 | 33.3 | 35.1 | **35.8** |
| 39 | 23.9 | 7.6 / 16.3 | 35.1 | 36.1 | 39.0 | **36.7** |
| 40 | 14.6 | 5.0 / 9.6 | 33.3 | 32.5 | 29.5 | **31.8** |
| 41 | 8.9 | 3.1 / 5.8 | 29.9 | 30.7 | 33.0 | **31.2** |
| 42 | 3.2 | 1.2 / 2.0 | 25.0 | 25.8 | 28.0 | **26.3** |
| 43 | 3.9 | 1.7 / 2.2 | 12.4 | 14.3 | 18.8 | **15.1** |
| 44 | 1.5 | 0.7 / 0.8 | 11.1 | 11.1 | 14.4 | **12.2** |
| 45 | 2.8 | 1.3 / 1.5 | 9.9 | 8.1 | 8.9 | **9.0** |
| Total amount: | 91.0 | 30.7 / 60.3 | | | | |

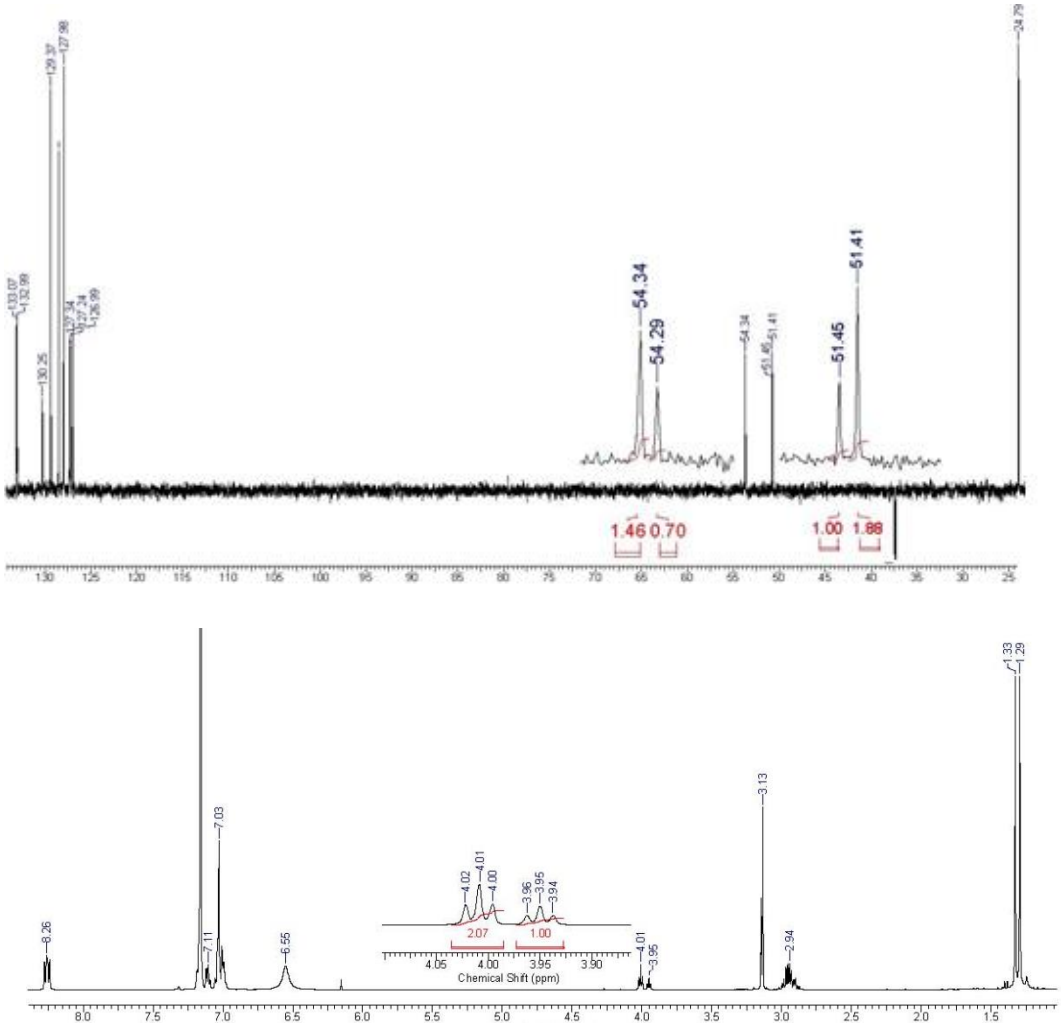


**Figure 6-ESI.** The $^{1}H$ and $^{13}C$ NMR spectra of **6** in the presence of enantiomerically pure **4**.

## SYNTHESIS OF BENCHMARK COMPOUNDS

Synthesis of compound **1**.

A 10 ml Schlenk flask was loaded with *(-)*-BisNapPhos [7] ligand (25 mg), [Pd(allyl)Cl]2 (3.6 mg) and toluene (1 mL). Reactor was degassed and backfilled with argon. After 30 min of stirring to the reactor was added solution of dimethyl malonate (100 mg) and (E)-1,3-diphenylallyl acetate (100 mg) in toluene (1 mL). Reactor was degassed and backfilled with argon again. After that BSA (192 mkL) was added to the reaction mixture. The solution was stirred at 40 °C for 10h. Solvents were evaporated to dryness, and column chromatography (hexane/acetone, 15:1, as eluent) of the residue gave **1** in quantitative yield and 49% ee. The enantiomeric composition and *R*- absolute configuration of the product were determined by the peak integration and elution order from chiral HPLC using a Chiralcel® OD-H column [8]. The spectra data of obtained compounds were identical to that found in literature [9]. $^1$H NMR ($CDCl_3$) δ: 3.5 (s, 3H), 3.7 (s, 3H), 4.0 (d, *J* = 11.0 Hz, 1H), 4.3 (dd, *J* = 11.0, 8.0 Hz, 1H), 6.3 (dd, *J* = 8.0, 15.7 Hz, 1H), 6.5 (d, *J* = 15.7 Hz, 1H), 7.2–7.3 (m, 10H).

Synthesis of compound **2**.

A round-bottom flask containing magnetic stir bar was charged with 15 mL of 0.3% aqueous SDS and $Na_2CO_3$ (318 mg). Then 1-bromo-2-methoxy-naphthalene, (237 mg) dissolved in a minimum amount of THF, 2-methoxy-1-naphthalenyl boronic acid (300 mg) and the pre-catalyst (prepared by premixing (*S*)-*BisNap*-Phos ligand (1 mol%) and $Pd(C_6H_5CN)_2Cl_2$ (0.5 mol%) in 1 mL of THF) were added. Reactor was degassed and backfilled with argon. The contents of flask was stirred at 60 °C for 16 hours. The product was extracted with methylene chloride or filtered. After drying the organic layer of MgSO4, the solvent was evaporated and the product was isolated by chromatography (hexane/acetone, 15:1, as eluent) to gave **2** in 96% yield and 41% ee. The enantiomeric excess of **2** was determined by an HPLC technique using a Chiralpak® AS-RH column, and the mobile phase $H_2O$ / $CH_3CN$ = 50 / 50. The spectra data of obtained compounds were identical to that found in literature [10 ]. $^1$H NMR ($CDCl_3$): δ = 3.78 (s, 6H, $OCH_3$), 7.10-7.12 (m, 2 H, CH), 7.21-7.23 (m, 2 H, CH), 7.31-7.34 (m, 2 H, CH), 7.47 (d, *J* = 9.1, 2 H, CH), 7.87-7.89 (m, 2 H, CH), 7.99 (d, *J* = 8.8, 2 H, CH).

Synthesis of compound **3**.

A 10 ml Schlenk flask was loaded with *4-nitrobenzaldehyde* (185 mg), technical grade acetone (6 mL). Reactor was degassed and backfilled with argon. After that to the reactor was added L-proline (34.5 mg). Reactor was degassed and backfilled with argon again. The solution was stirred at 25 °C for 3 days. To the reaction mixture 10 mL of saturated aqueous solution of NH4Cl was added, and product was extracted with 15 mL of ethyl acetate. Organic phase was separated and dried over MgSO4. Solvents were evaporated to dryness, and column chromatography (hexane/ethyl acetate/ methanol = 5/3/0.2, as eluent) of the residue gave **2** in 73% yield and 47% ee. The optical purity of synthesized compound **3** was determined by an HPLC technique using a Chiralpak® AD-RH column, and the $CH_3CN$ / $H_2O$ = 30 / 70 mobile phase. The spectra data of obtained compounds were identical to that found in literature

[12]. $^{1}$H NMR (CDCl3): $\delta$ = 2.3 (s, 3H) , 2.9 (m, 2 H), 3.6 (d, *J* = 3.0 Hz, 1 H), 5.2-5.3 (m, 1 H), 7.6 (d, *J* = 8.5 Hz, 1 H), 8.2 (d, *J* = 8.5 Hz, 1 H).

Synthesis of compound **4**.

The chosen model compound was earlier synthesized in accordance with the literature procedure [13].

Synthesis of compound **5**.

A 50 mL flask equipped with reflux condenser was loaded with phenylalanine (3 g), methanol (15 mL) and acetic anhydride (5 g). The reaction mixture was stirred at 65 $^{o}$C overnight. Solvents were evaporated to dryness and solid residual was recrystallized from ethyl acetate to give **5** in 80% yield. The enantiomeric composition of the consecutive fractions was determined be means of a chiral HPLC Chiralpak® OJ-RH column, with the mobile phase using $H_2O$ / $CH_3CN$ = 85 / 15 at the flow rate equal to 0.3 mL/min. The spectra data of obtained compounds were identical to that found in literature [14]. $^{1}$H NMR (CD3OD): 1.9 (s, 3H), 2.3 (dd, *J* = 14.0, 9.0 Hz, 1H), 3.2 (dd, *J* = 14.0, 5.0 Hz, 1H), 4.7 – 4.6 (m, 1H), 7.4 – 7.1 (m, 5H).

To obtain the compounds of required ee, the corresponding amounts of racemic **5** and optically pure **5** obtained as presented above were mixed.

Synthesis of compound **6**.

A 50 mL flask was loaded with phenylalanine of required optical purity (3 g), methanol (15 mL) and cooled to 0°C in an ice bath. Thionyl chloride (6 mL) was added dropwise keeping the reaction in continuous stirring at 0°C. Next, the reaction mixture warmed to room temperature and stirred for next 1 h. The solvents were removed under reduced pressure to yield the hydrochloride salt of **6** in quantitative yield. The compound **6** was liberated from the salt before the SDS experiments. 1 g of **6***HCl was shacked in separation funnel with 20 mL DCM and 10 ml a saturated $Na_2CO_3$. Organic phase was separated, dried over $Na_2SO_4$, and solvent was evaporated off under reduced pressure, while residue dried in vacuum for few hours. The optical purity of the fractions was determined based on the $^{1}$H and $^{13}$C NMR techniques using, as CDA, 100 mol% of enantiomericaly pure **4**. The spectra data of obtained compounds were identical to that found in literature [15]. $^{1}$H NMR ($CDCl_3$): 1.49 (bs, 2H), 2.8 (dd, *J* = 9.0, 13.5 Hz, 1H), 3.1 (dd, *J* = 5.0, 13.5 Hz, 1H), 3.7 (s, 3H), 3.7 (m, 1H), 7.2-7.3 (m, 5H).

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