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Supporting Information

Asymmetric Synthesis of Fully Substituted Cyclopentane-Oxindoles through an Organocatalytic Triple Michael Domino Reaction

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CONTENTS

1. General Information

Flash chromatography was carried out with Merck silica gel 60 (230-240 mesh). Analytical TLC was performed with aluminium-backed silica gel sheets 60 F254 (Merck), and the products were visualized by UV detection. Optical rotation values were measured on a Perkin-Elmer 241 polarimeter. Microanalyses were performed with a Vario EL element analyser. High resolution mass spectra (HRMS) were acquired on a ThermoFisher Scientific LTQ-Orbitrap XL. IR spectra (cm^{-1}) were taken on a PerkinElmer Spectrum 100 FT-IR Spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on Inova 400 or Agilent VNMRS 600 spectrometers. Chemical shifts (δ) are given in ppm relative to solvent residual peak ($CDCl_3$, δ = 7.26 ppm) as external standard. Analytical HPLC was performed on a Hewlett-Packard 1100 Series instrument using chiral stationary phases [Daicel IC, Daicel AD, Daicel IA, Merck (s,s)-Whelk 01]. Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), bs (broad singlet).

2. Materials

N-Boc-oxindoles **1a-f** were synthesized according to the known procedures.[1] Nitrodiene **2** was prepared according to the literature.[2] Chloroform (analytical grade) was bought from Fisher. Other solvents were dried and distilled prior to use. All other chemicals were used as purchased from commercial suppliers without further purification.

The racemic samples of **4a**, **4b**, **4d**, **4e**, **4f**, **4g**, **4h**, **4i** and **4j** were prepared using pyrrolidine as catalyst. The racemic samples of **4c**, **4k**, **4l**, **4m**, were prepared using a mixture of (R+S)-catalyst A. The racemic sample of **6** was prepared according to the literature.[3]

Procedure for the synthesis of compound **6**: To a 25 mL round bottom flask, equipped with a stirring bar, was added compound **4a** (112 mg, 0.17 mmol), trifluoroacetic acid (0.8 ml) and DCM (8 mL). After stirring for 15 h, a saturated aqueous $NaHCO_3$ solution (20 mL) solution was added. The mixture was extracted with DCM (3 x 50 mL) and washed with brine. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification was performed by column chromatography on silica gel (pentane/ethyl acetate = 3:1 as eluent) to provide the desired product **6** as a colorless solid in 94% yield and with 95% ee (89 mg, 0.16 mmol).

3. General Procedure

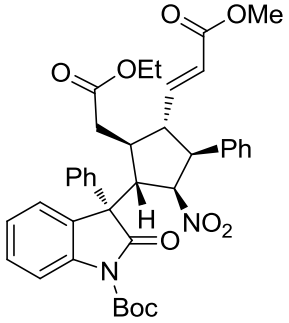
General procedure for the organocatalytic domino reaction (described for **4a** as a typical example):
a) Method A: A 10 mL glass vial equipped with a magnetic stirring bar was charged with **1a** (154.6 mg, 0.5 mmol), **2** (86 mg, 0.5 mmol), **3a** (66 mg, 0.5 mmol) and catalyst **A** (81.5 mg, 0.25 mmol). After adding $CHCl_3$ (4 mL), the reaction tube was purged using an argon flow for 1 min, then covered with a teflon-coated screw cap. The reaction mixture was stirred at room temperature for 22 h. After addition of wittig reagent **5** (250 mg, 0.75 mmol) and purging using an argon flow for 1 min, the mixture was stirred for another 5 h. The resulting solution was then directly applied to flash chromatography (at first pentane/ethyl acetate = 10:1, then pentane/ethyl acetate = 5:1 as eluent) to get the desired product **4a** as a yellow solid (180 mg, 54% yield, 15:1 dr, 98% ee).

b) Method B: A 10 mL glass vial equipped with a magnetic stirring bar was charged with **1a** (51.5 mg, 0.17 mmol), **2** (28.7 mg, 0.17 mmol), **3a** (22 mg, 0.17 mmol) and catalyst **A** (81.5 mg, 0.25 mmol) (starting materials **1a**, **2** and **3a** were divided into three portions). The reaction tube was purged using an argon flow for 1 min, then covered with a teflon-coated screw cap after adding $CHCl_3$ (4 mL). After stirring at room temperature for 3 h, the second portion of **1a** (51.5 mg, 0.17 mmol), **2** (28.7 mg, 0.17 mmol) and **3a** (22 mg, 0.17 mmol) was added in the reaction tube. After purging using an argon flow for 1 min, the mixture was stirred for another 3 h. After that, the third portion of **1a** (51.5 mg, 0.17 mmol), **2** (28.7 mg, 0.17 mmol) and **3a** (22 mg, 0.17 mmol) was added into the reaction mixture, which was stirred for another 16 h after purging using an argon flow for 1 min. Then the first portion of Wittig reagent **5** (83.5 mg, 0.25 mmol) was added into the reaction tube. The mixture was stirred for 3 h after purging using an argon flow for 1 min. After that, the second portion of Wittig reagent **5** (83.5 mg, 0.25 mmol) was added into the reaction mixture. The mixture was stirred for another 3 h after purging using an argon flow for 1 min. The resulting solution was then directly applied to flash chromatography (at first pentane/ethyl acetate = 10:1, then pentane/ethyl acetate = 5:1 as eluent) to get product **4a** as a yellow solid (209 mg, 63% yield, 15:1 dr, 99% ee).

For both cases, the major diastereoisomer could be isolated as a colorless solid by using a preparative TLC plate (hexane/isopropanol = 15:1 as eluent).

4. Analytical data of the products

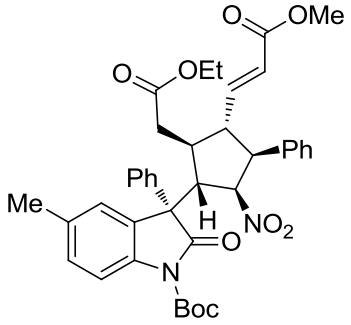
(*S*)-tert-Butyl-3-{(1*S*, 2*S*, 3*S*, 4*S*, 5*R*)-2-(2-ethoxy-2-oxoethyl)-3-[(*E*)-3-methoxy-3-oxoprop-1-en-1-yl]-5-nitro-4-phenylcyclopentyl}-2-oxo-3-phenylindoline-1-carboxylate (4a)



The compound was prepared according to the general procedure (method B). The product was obtained as a colorless solid, yield 63%, m.p. 74-76 ºC. The ee (99%) was measured by HPLC using a chiral stationary phase [Daicel IC, n-heptane:EtOH = 97:3, 0.7 mL/min, t_R = 20.66 min (major), 15.39 min (minor)]. $[\alpha]_D^{22}$ = −77.9 (c = 0.66, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.2 Hz, 1H), 7.52-7.50 (m, 1H), 7.38-7.36 (m, 4H), 7.33-7.28 (m, 3H), 7.24-7.20 (m, 3H), 7.00 (d, *J* = 6.7 Hz, 2H), 6.30 (dd, *J* = 15.5 Hz, 9.5 Hz, 1H), 5.75 (d, *J* = 15.6 Hz, 1H), 4.86 (d, *J* = 6.4 Hz, 1H), 4.05-4.01 (m, 3H), 3.58 (s, 3H), 3.47-3.41 (m, 1H), 3.30-3.26 (m, 1H), 2.52 (d, *J* = 14.0 Hz, 1H), 2.32-2.27 (m, 2H), 1.61 (s, 9H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.9, 171.0, 165.9, 148.6, 146.5, 140.6, 136.6, 133.2, 130.0, 129.2, 128.8, 128.6, 128.3, 127.7, 127.5, 124.9, 124.6, 124.1, 116.0, 94.8, 85.0, 60.6, 58.3, 55.0, 54.8, 51.4, 50.4, 42.1, 37.6, 29.7, 28.0, 14.0. IR: 2970, 1736, 1553, 1457, 1365, 1218, 1150, 987, 905, 845, 736. HRMS (ESI): calcd for $C_{38}H_{40}N_2O_9Na$: 691.2632; found: 691.2631. Anal. Calcd for $C_{38}H_{40}N_2O_9$: C, 68.25; H, 6.03; N, 4.19; Found: C, 67.95; H, 6.04; N, 4.16.

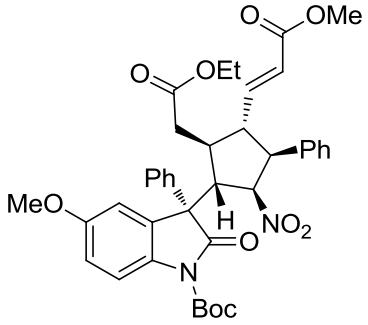
(*S*)-tert-Butyl-3-{(1*S*, 2*S*, 3*S*, 4*S*, 5*R*)-2-(2-ethoxy-2-oxoethyl)-3-[(*E*)-3-methoxy-3-oxoprop-1-en-1-yl]-5-nitro-4-phenylcyclopentyl}-5-methyl-2-oxo-3-phenylindoline-1-carboxylate (4b)



The compound was prepared according to the general procedure (method B). The product was obtained as a colorless solid, yield 63%, m.p. 80-82 °C. The ee (98%) was measured by HPLC using a chiral stationary phase [Daicel AD, n-heptane:isopropanol = 97:3, 0.3 mL/min, t_R = 45.76 min (major), 59.97 min (minor)]. $[\alpha]_D^{22}$ = −77.5 (c = 1.06, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.33-7.28 (m, 4H), 7.24-7.20 (m, 3H), 7.18 (s, 1H), 6.97 (d, *J* = 6.8 Hz, 2H), 6.29 (dd, *J* = 15.5 Hz, 9.6 Hz, 1H), 5.75 (d, *J* = 15.6 Hz, 1H), 4.87 (d, *J* = 6.5 Hz, 1H), 4.04-4.00 (m, 3H), 3.58 (s, 3H), 3.46-3.40 (m, 1H), 3.25-3.22 (m, 1H), 2.54 (d, *J* = 15.5 Hz, 1H), 2.49 (s, 3H), 2.33 (br, 1H), 2.24 (br, 1H), 1.60 (s, 9H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 175.0, 171.0, 166.0, 148.7, 146.6, 138.3, 136.8, 134.6, 133.2, 130.5, 129.2, 128.8, 128.5, 128.3, 127.7, 127.6, 125.2, 124.1, 115.7, 94.8, 84.8, 60.6, 58.4, 55.1, 54.6, 51.4, 50.4, 42.0, 37.7, 29.7, 28.0, 21.5, 14.0. IR: 2939, 1731, 1550, 1470, 1344, 1245, 1155, 1030, 845, 747. HRMS (ESI) calcd for $C_{39}H_{42}N_2O_9Na$: 705.2788; found: 705.2765.

(S)-tert-Butyl-3-{(1*S*, 2*S*, 3*S*, 4*S*, 5*R*)-2-(2-ethoxy-2-oxoethyl)-3-[(*E*)-3-methoxy-3-oxoprop-1-en-1-yl]-5-nitro-4-phenylcyclopentyl}-5-methoxy-2-oxo-3-phenylindoline-1-carboxylate (4c)

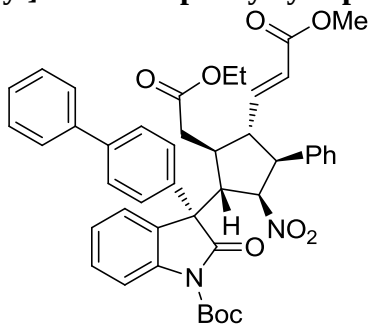


The compound was prepared according to the general procedure (method B). The product was obtained as a colorless solid, yield 72%, m.p. 83-85 °C. The ee (97%) was measured by HPLC using a chiral stationary phase [Daicel IA, n-heptane:isopropanol = 95:5, 0.7 mL/min, t_R = 24.37 min (major), 38.75 min (minor)]. $[\alpha]_D^{22}$ = −58.7 (c = 2.07, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 9.0 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 2H), 7.32-7.28 (m, 3H), 7.24-7.20 (m, 3H), 7.03-7.00 (m, 3H), 6.91 (d, *J* = 2.6 Hz, 1H), 6.32 (dd, *J* = 15.5 Hz, 9.5 Hz, 1H), 5.77 (d, *J* = 15.6 Hz, 1H), 4.86 (d, *J* = 6.3 Hz, 1H), 4.05-4.00 (m, 3H), 3.90 (s, 3H), 3.58 (s, 3H), 3.47-3.41 (m, 1H), 3.32-3.28 (m, 1H), 2.54 (d, *J* = 15.7 Hz, 1H), 2.34 (br, 1H), 2.25 (br, 1H), 1.60 (s, 9H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.9, 171.0, 166.0, 157.1, 148.7, 146.6, 136.7, 133.9, 133.2, 129.2, 128.8, 128.6, 128.3, 127.7, 127.5, 124.2, 116.8, 113.9, 111.6, 94.8, 84.8, 60.6, 58.6,

55.8, 55.0, 54.7, 51.5, 50.5, 42.0, 37.7, 29.7, 28.0, 14.0. IR: 2940, 1732, 1554, 1479, 1360, 1237, 1155, 1031, 839, 702. HRMS (ESI) calcd for $C_{39}H_{42}N_2O_{10}Na$: 721.2737; found: 721.2703.

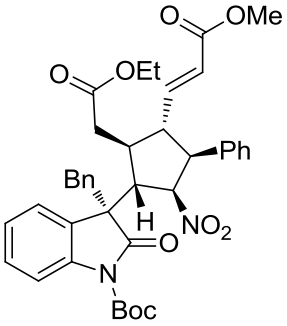
(*S*)-tert-Butyl-3-{(1*S*, 2*S*, 3*S*, 4*S*, 5*R*)-2-(2-ethoxy-2-oxoethyl)-3-[(*E*)-3-methoxy-3-oxoprop-1-en-1-yl]-5-nitro-4-phenylcyclopentyl}-2-oxo-3-biphenylindoline-1-carboxylate (4d)



The compound was prepared according to the general procedure (method A). The product was obtained as a colorless solid, yield 57%, m.p. 90-92 °C. The ee (99%) was measured by HPLC using a chiral stationary phase [Merck (s,s)-Whelk 01, n-heptane:EtOH = 7:3, 0.7 mL/min, t_R = 14.13 min (major), 18.75 min (minor)]. $[\alpha]_D^{22}$ = −70.8 (c = 1.12, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.2 Hz, 1H), 7.54-7.50 (m, 5H), 7.42-7.39 (m, 6H), 7.32 (m, *J* = 7.3 Hz, 1H), 7.25-7.21 (m, 3H), 7.01 (d, *J* = 6.8 Hz, 2H), 6.32-6.28 (m, 1H), 5.76 (d, *J* = 15.6 Hz, 1H), 4.93 (d, *J* = 6.0 Hz, 1H), 4.08 (dd, *J* = 8.4 Hz, 2.5 Hz, 1H), 4.05-4.01 (m, 2H), 3.58 (s, 3H), 3.48-3.43 (m, 1H), 3.31-3.28 (m, 1H), 2.58 (d, *J* = 14.5 Hz, 1H), 2.38-2.34 (m, 1H), 2.27 (bs, 1H), 1.62 (s, 9H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.9, 171.0, 165.9, 148.6, 146.5, 141.5, 140.7, 139.9, 135.6, 133.2, 130.1, 128.8 (2C), 128.3, 128.0, 127.8, 127.7, 127.6, 127.4, 125.0, 124.6, 124.1, 116.0, 94.9, 85.0, 60.6, 58.2, 55.0, 54.7, 51.5, 50.4, 42.1, 37.8, 29.7, 28.0, 14.0. IR: 2933, 1730, 1553, 1464, 1347, 1233, 1152, 1028, 841, 749, 699. HRMS (ESI) calcd for $C_{44}H_{44}N_2O_9Na$: 767.2945; found: 767.2895.

(*R*)-tert-Butyl-3-benzyl-3-{(1*S*, 2*S*, 3*S*, 4*S*, 5*R*)-2-(2-ethoxy-2-oxoethyl)-3-[(*E*)-3-methoxy-3-oxoprop-1-en-1-yl]-5-nitro-4-phenylcyclopentyl}-2-oxoindoline-1-carboxylate (4e)

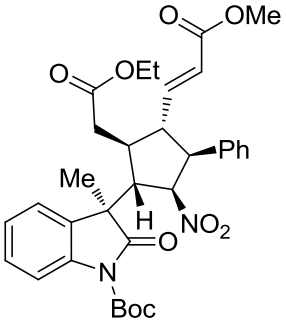


The compound was prepared according to the general procedure (method B). The product was obtained as a colorless solid, yield 30%, m.p. 65-67 °C. The ee (99%) was measured by HPLC using a chiral stationary phase [Daicel IA, n-heptane:EtOH = 7:3, 0.7 mL/min, t_R = 12.29 min (major), 9.34 min (minor)]. $[\alpha]_D^{22}$ = −17.6 (c = 0.46, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.24-7.21 (m, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.03-6.97 (m, 5H), 6.73 (q, *J* = 7.8 Hz, 3H), 5.64 (d, *J* = 15.8 Hz, 1H), 4.43 (t, *J* = 7.9 Hz, 1H), 4.20-4.08 (m, 2H), 3.64-3.58 (m, 5H), 3.45 (d, *J* = 12.8 Hz, 2H), 3.39 (dd, *J* = 7.1 Hz, 3.0

Hz, 1H), 3.35-3.30 (m, 1H), 3.02 (d, *J* = 12.8 Hz, 1H), 2.77-2.74 (m, 1H), 2.63-2.60 (m, 1H), 1.55 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 176.4, 171.7, 165.9, 148.0, 143.8, 139.8, 136.0, 133.9, 129.7, 129.4, 129.2, 128.3, 127.7, 127.0, 126.9, 124.7, 124.6, 123.3, 115.2, 96.0, 84.5, 61.0, 56.6, 55.5, 54.4, 51.5, 48.1, 42.9, 39.7, 37.7, 29.7, 28.0, 14.1. IR: 2931, 1674, 1450, 1291, 1221, 1145, 974, 851, 753, 693. HRMS (ESI) calcd for $C_{39}H_{42}N_2O_9Na$: 705.2788; found: 705.2754.

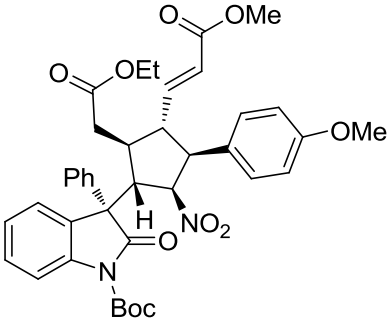
(*R*)-tert-Butyl-3-{(1*S*, 2*S*, 3*S*, 4*S*, 5*R*)-2-(2-ethoxy-2-oxoethyl)-3-[(*E*)-3-methoxy-3-oxoprop-1-en-1-yl]-5-nitro-4-phenylcyclopentyl}-3-methyl-2-oxoindoline-1-carboxylate (4f)



The compound was prepared according to the general procedure (method A). The product was obtained as a colorless solid, yield 44%, m.p. 57-59 °C. The ee (91%) was measured by HPLC using a chiral stationary phase [Daicel IA, n-heptane:isopropanol = 95:5, 0.7 mL/min, t_R = 22.17 min (major), 27.99 min (minor)]. $[\alpha]_D^{22}$ = −5.8 (c = 0.87, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.2 Hz, 1H), 7.35-7.33 (m, 1H), 7.27-7.23 (m, 3H), 7.17-7.16 (m, 2H), 7.00 (d, *J* = 6.8 Hz, 2H), 6.67 (dd, *J* = 15.8 Hz, 7.2 Hz, 1H), 5.57 (d, *J* = 15.6 Hz, 1H), 4.43-4.40 (m, 1H), 4.17-4.10 (m, 2H), 3.60 (s, 3H), 3.58-3.55 (m, 1H), 3.17-3.14 (m, 3H), 2.67 (dd, *J* = 15.3 Hz, 6.6 Hz, 1H), 2.53 (dd, *J* = 15.4 Hz, 6.9 Hz, 1H), 1.67 (s, 9H), 1.51 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 177.4, 171.6, 165.8, 148.7, 143.7, 139.0, 136.1, 129.7, 129.3, 129.2, 128.3, 126.9, 125.1, 124.5, 122.8, 115.4, 95.5, 85.0, 60.9, 56.3, 54.3, 51.5, 49.7, 48.1, 39.5, 37.5, 30.9, 28.1, 22.5, 14.1. IR: 2976, 1729, 1553, 1478, 1240, 1153, 1031, 838, 748. HRMS (ESI) calcd for $C_{33}H_{38}N_2O_9Na$: 629.2475; found: 629.2448.

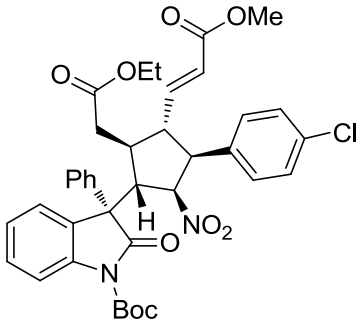
(*S*)-tert-Butyl-3-{(1*S*, 2*S*, 3*S*, 4*S*, 5*R*)-2-(2-ethoxy-2-oxoethyl)-3-[(*E*)-3-methoxy-3-oxoprop-1-en-1-yl]-4-(4-methoxyphenyl)-5-nitrocyclopentyl}-2-oxo-3-phenylindoline-1-carboxylate (4g)



The compound was prepared according to the general procedure (method B). The product was obtained as a colorless solid, yield 61%, m.p. 90-92 °C. The ee (99%) was measured by HPLC using a chiral stationary phase [Daicel IC, n-heptane:isopropanol = 7:3, 0.5 mL/min, t_R = 12.51 min (major), 9.36 min (minor)]. $[\alpha]_D^{22}$ = −66.9 (c = 0.48, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.2 Hz, 1H), 7.50 (p, *J* = 4.6 Hz, 1H), 7.37-7.35 (m, 4H), 7.32-7.28 (m, 3H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.30-6.26 (m, 1H), 5.73 (d, *J* = 15.6 Hz, 2H), 4.82 (d, *J* = 6.4 Hz, 1H), 4.04-4.00 (m, 3H), 3.72 (s, 3H), 3.58 (s, 3H), 3.40-3.34 (m, 1H), 3.24-3.21 (m, 1H), 2.51 (d, *J* = 14.6 Hz, 1H), 2.30-2.24 (br, 1H), 1.61 (s, 9H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 175.0, 171.0, 165.9, 159.4, 148.6, 146.7, 140.5, 136.7, 130.0, 129.2, 128.8, 128.6, 127.5, 125.1, 125.0, 124.5, 124.0, 116.0, 114.2, 94.8, 85.0, 60.6, 58.3, 55.1, 54.8, 54.4, 51.4, 50.7, 42.0, 37.7, 29.7, 28.0, 14.0. IR: 2927, 1728, 1553, 1462, 1248, 1154, 1031, 843, 752. HRMS (ESI) calcd for $C_{39}H_{42}N_2O_{10}Na$: 721.2737; found: 721.2678.

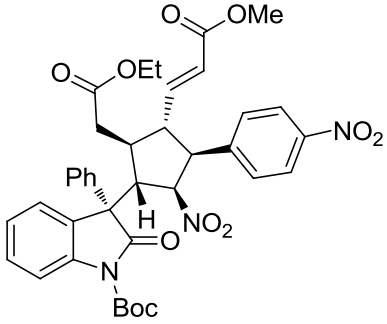
(*S*)-tert-Butyl-3-{(1*S*, 2*S*, 3*S*, 4*S*, 5*R*)-4-(4-chlorophenyl)-2-(2-ethoxy-2-oxoethyl)-3-[(*E*)-3-methoxy-3-oxoprop-1-en-1-yl]-5-nitrocyclopentyl}-2-oxo-3-phenylindoline-1-carboxylate (4h)



The compound was prepared according to the general procedure (method B). The product was obtained as a colorless solid, yield 65%, m.p. 89-91 ^{o}C. The ee (99%) was measured by HPLC using a chiral stationary phase [Daicel IC, n-heptane:EtOH = 97:3, 0.7 mL/min, t_R = 17.41 min (major), 15.52 min (minor)]. $[\alpha]_D^{22}$ = −62.3 (c = 1.43, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.2 Hz, 1H), 7.52-7.49 (m, 1H), 7.38-7.36 (m, 4H), 7.33-7.29 (m, 3H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.31-6.27 (m, 1H), 5.74 (d, *J* = 15.6 Hz, 1H), 4.82 (d, *J* = 6.3 Hz, 1H), 4.05-4.01 (m, 3H), 3.59 (s, 3H), 3.42-3.36 (m, 1H), 3.26-3.23 (m, 1H), 2.47 (d, *J* = 14.1 Hz, 1H), 2.26 (bs, 2H), 1.61 (s, 9H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.9, 170.9, 165.8, 148.6, 146.1, 140.5, 136.4, 134.3, 131.8, 130.0, 129.2, 129.1, 129.0, 128.7, 127.5, 125.0, 124.4, 124.3, 116.0, 94.6, 85.1, 60.6, 58.2, 54.7, 54.2, 51.5, 50.5, 42.0, 37.4, 29.7, 28.0, 14.0. IR: 2941, 1729, 1554, 1467, 1346, 1285, 1247, 1150, 1094, 1019, 845, 757, 724. HRMS (ESI) calcd for $C_{38}H_{39}ClN_2O_9Na$: 725.2242; found: 725.2222.

(*S*)-tert-Butyl-3-{(1*S*, 2*S*, 3*S*, 4*S*, 5*R*)-2-(2-ethoxy-2-oxoethyl)-3-[(*E*)-3-methoxy-3-oxoprop-1-en-1-yl]-5-nitro-4-(4-nitrophenyl)cyclopentyl}-2-oxo-3-phenylindoline-1-carboxylate (4i)

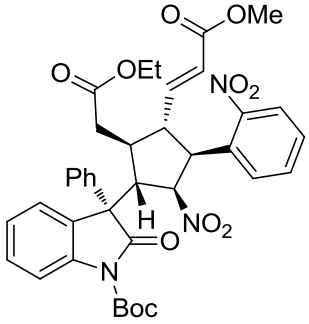


The compound was prepared according to the general procedure (method A). The product was obtained as a yellow solid, yield 61%, m.p. 93-95 ^{o}C. The ee (99%) was measured by HPLC using a chiral

stationary phase [Daicel IA, n-heptane:EtOH = 7:3, 0.7 mL/min, t_R = 9.45 min (major), 15.28 min (minor)]. $[\alpha]_D^{22}$ = −53.0 (c = 0.74, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.7 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.52-7.49 (m, 1H), 7.40-7.36 (m, 4H), 7.34-7.30 (m, 3H), 7.19 (d, *J* = 8.7 Hz, 2H), 6.34-6.30 (m, 1H), 5.78 (d, *J* = 15.6 Hz, 1H), 4.84 (d, *J* = 5.7 Hz, 1H), 4.09-4.03 (m, 3H), 3.59 (s, 3H), 3.51-3.45 (m, 1H), 3.41-3.38 (m, 1H), 2.43 (d, *J* = 14.8 Hz, 2H), 2.20 (bs, 1H), 1.62 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 175.0, 170.8, 165.7, 148.5, 147.8, 145.5, 140.7, 140.3, 136.2, 130.1, 129.3, 128.9, 128.8, 127.4, 125.0, 124.7, 124.3, 123.9, 116.1, 94.4, 85.2, 60.7, 58.1, 54.5, 54.1, 51.6, 50.3, 42.1, 37.0, 29.7, 28.0, 14.0. IR: 2940, 2322, 2077, 1729, 1535, 1464, 1345, 1243, 1152, 1027, 854, 748. HRMS (ESI) calcd for $C_{38}H_{39}N_3O_{11}Na$: 736.2482; found: 736.2452.

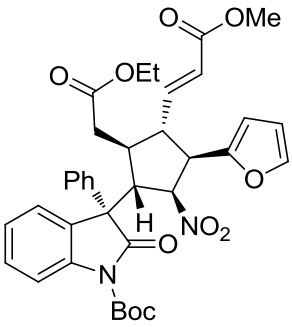
(*S*)-tert-Butyl-3-{(1*S*, 2*S*, 3*S*, 4*S*, 5*R*)-2-(2-ethoxy-2-oxoethyl)-3-[(*E*)-3-methoxy-3-oxoprop-1-en-1-yl]-5-nitro-4-(2-nitrophenyl)cyclopentyl}-2-oxo-3-phenylindoline-1-carboxylate (4j)



The compound was prepared according to the general procedure (method B). The product was obtained as a yellow solid, yield 61%, m.p. 89-91 ^{o}C. The ee (97%) was measured by HPLC using a chiral stationary phase [Daicel IA, n-heptane:EtOH = 9:1, 1.0 mL/min, t_R = 10.51 min (major), 9.34 min (minor)]. $[\alpha]_D^{22}$ = −207.3 (c = 1.25, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.53-7.48 (m, 2H), 7.43-7.38 (m, 4H), 7.32-7.27 (m, 3H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.27-6.23 (m, 1H), 5.78 (d, *J* = 15.6 Hz, 1H), 5.31 (br, 1H), 4.18 (dd, *J* = 8.7 Hz, 2.4 Hz, 1H), 4.08-3.99 (m, 2H), 3.86 (dd, *J* = 12.5 Hz, 7.9 Hz, 1H), 3.58 (s, 3H), 3.55-3.50 (m, 1H), 2.54 (d, *J* = 12.5 Hz, 1H), 2.34-2.22 (m, 2H), 1.62 (s, 9H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 175.1, 170.8, 165.6, 149.5, 148.6, 145.4, 140.3, 136.7, 133.9, 129.9, 129.3, 129.2, 128.8, 128.6, 127.5, 125.6, 125.3, 124.9 (2C), 115.8, 93.4, 84.9, 60.7, 58.0, 54.8, 51.6, 50.4, 49.8, 41.7, 36.9, 29.6, 28.0, 14.0. IR: 2980, 1730, 1535, 1464, 1344, 1285, 1152, 1025, 848, 732. HRMS (ESI) calcd for $C_{38}H_{39}N_3O_{11}Na$: 736.2482; found: 736.2487.

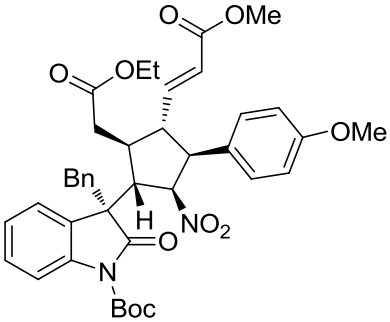
(S)-tert-Butyl-3-{(1*S*, 2*S*, 3*S*, 4*S*, 5*R*)-2-(2-ethoxy-2-oxoethyl)-4-(furan-2-yl)-3-[(*E*)-3-methoxy-3-oxoprop-1-en-1-yl]-5-nitrocyclopentyl}-2-oxo-3-phenylindoline-1-carboxylate (4k)



The compound was prepared according to the general procedure (method B). The product was obtained as a pink solid, yield 47%, m.p. 75-77 ^{o}C. The ee (99%) was measured by HPLC using a chiral stationary phase [Daicel IC, n-heptane:isopropanol = 9:1, 0.7 mL/min, t_R = 15.62 min (major), 11.26 min (minor)]. $[\alpha]_D^{22}$ = −70.5 (c = 0.29, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.2 Hz, 1H), 7.51-7.48 (m, 1H), 7.37-7.35 (m, 4H), 7.32-7.30 (m, 3H), 7.24 (d, *J* = 1.6 Hz, 1H), 6.34-6.30 (m, 1H), 6.21-6.20 (m, 1H), 6.01 (d, *J* = 3.2 Hz, 1H), 5.75 (d, *J* = 15.6 Hz, 1H), 4.91 (d, *J* = 6.7 Hz, 1H), 4.03-4.00 (m, 3H), 3.62 (s, 3H), 3.41-3.37 (m, 1H), 3.28-3.23 (m, 1H), 2.47 (br, 1H), 2.26 (br, 2H), 1.61 (s, 9H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.9, 170.9, 165.9, 148.6, 147.9, 146.1, 142.7, 136.5, 130.0, 129.2, 128.6, 127.5, 125.0, 124.5, 124.2, 116.0, 110.5, 108.4, 92.6, 85.0, 60.6, 58.2, 54.9, 51.5, 50.8, 48.9, 41.9, 37.7, 29.7, 28.1, 28.0, 14.0. IR: 2926, 1730, 1555, 1464, 1247, 1151, 1019, 843, 740. HRMS (ESI) calcd for $C_{36}H_{38}N_2O_{10}Na$: 681.2424; found: 681.2385.

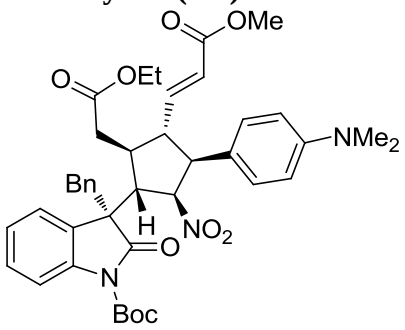
(*R*)-tert-Butyl-3-benzyl-3-{(1*S*, 2*S*, 3*S*, 4*S*, 5*R*)-2-(2-ethoxy-2-oxoethyl)-3-[(*E*)-3-methoxy-3-oxoprop-1-en-1-yl]-4-(4-methoxyphenyl)-5-nitrocyclopentyl}-2-oxolindoline-1-carboxylate (4l)



The compound was prepared according to the general procedure (method B). The product was obtained as a colorless solid, yield 47%, m.p. 71-73 ^{o}C. The ee (99%) was measured by HPLC using a chiral stationary phase [Daicel IA, n-heptane:isopropanol = 9:1, 1.0 mL/min, t_R = 28.10 min (major), 10.69 min (minor)]. $[\alpha]_D^{22}$ = −29.2 (c = 0.42, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 7.1 Hz, 1H), 7.24-7.21 (m, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.98 (t, *J* = 7.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.73 (dd, *J* = 7.7 Hz, 2.4Hz, 2H), 5.63 (d, *J* = 15.8 Hz, 1H), 4.39 (t, *J* = 8.4 Hz, 1H), 4.18-4.10 (m, 2H), 3.74 (s, 3H), 3.63 (s, 3H), 3.60-3.54 (m, 2H), 3.44 (d, *J* = 12.8 Hz, 2H), 3.37 (dd, *J* = 7.2 Hz, 3.0 Hz, 1H), 3.29-3.24 (m, 1H), 3.01 (d, *J* = 12.8 Hz, 1H), 2.76-2.72 (m, 1H), 2.62-2.58 (m, 1H), 1.55 (s, 9H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 176.4, 171.7, 165.9, 159.4, 148.0, 143.9, 139.8, 133.9, 129.7, 129.3, 128.0, 127.9, 127.4, 127.0, 126.9, 124.6, 123.3, 115.2, 114.6, 96.2, 84.5, 60.9, 56.6, 55.4, 55.2, 53.8, 51.5, 48.1, 42.9, 39.6, 37.8, 29.7, 28.0, 14.1. IR: 2976, 1729, 1551, 1463, 1354, 1247, 1153, 1025, 837, 752, 702. HRMS (ESI) calcd for $C_{40}H_{44}N_2O_{10}Na$: 735.2894; found: 735.2853.

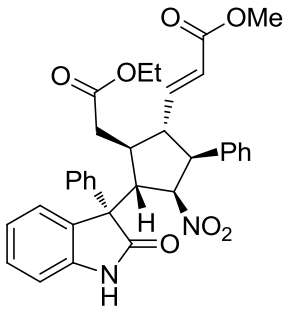
(R)-tert-Butyl-3-benzyl-3-{(1*S*, 2*S*, 3*S*, 4*S*, 5*R*)-4-(4-dimethylaminophenyl)-2-(2-ethoxy-2-oxoethyl)-3-[(*E*)-3-methoxy-3-oxoprop-1-en-1-yl]-5-nitrocyclopentyl}-2-oxolindoline-1-carboxylate (4m)



The compound was prepared according to the general procedure (method B). The product was obtained as a yellow solid, yield 63%, m.p. 70-72 ^{o}C. The ee (99%) was measured by HPLC using a chiral stationary phase [Daicel IA, n-heptane:isopropanol = 95:5, 0.7 mL/min, t_R = 49.06 min (major), 23.21 min (minor)]. $[\alpha]_D^{22}$ = −58.9 (c = 0.28, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.22 (td, *J* = 7.7 Hz, 1.2 Hz, 1H), 7.17 (td, *J* = 7.5 Hz, 0.9 Hz, 1H), 7.04-7.01 (m, 1H), 6.99-6.96 (m, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.73-6.71 (m, 2H), 6.59 (d, *J* = 8.0 Hz, 2H), 5.65 (d, *J* = 15.8 Hz, 1H), 4.41 (brs, 1H), 4.18-4.08 (m, 2H), 3.62 (s, 3H), 3.59-3.51 (m, 2H), 3.42 (d, *J* = 12.8 Hz, 1H), 3.35 (dd, *J* = 7.1 Hz, 2.3 Hz, 2H), 3.26-3.21 (m, 1H), 3.01 (d, *J* = 12.9 Hz, 1H), 2.89 (s, 6H), 2.75-2.71 (m, 1H), 2.59 (dd, *J* = 15.4 Hz, 7.2 Hz, 1H), 1.55 (s, 9H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 175.1, 170.8, 165.6, 150.2, 149.5, 148.6, 145.4, 140.3, 136.7, 133.9, 129.9, 129.3, 129.2, 128.8, 128.6, 127.5, 125.6, 125.3, 124.9, 115.8, 93.4, 84.9, 60.7, 58.0, 54.8, 51.6, 50.4, 49.8, 41.7, 36.9, 30.9, 29.7, 28.0, 14.0. IR: 2927, 1731, 1550, 1469, 1352, 1246, 1154, 1032, 831, 749. HRMS (ESI) calcd for $C_{41}H_{47}N_3O_9Na$: 748.3210; found: 748.3173.

3-{(1*S*,2*S*,3*S*,4*R*,5*S*)-2-(2-Ethoxy-2-oxoethyl)-4-nitro-3-[(*S*)-2-oxo-3-phenylindolin-3-yl]-5-phenylcy-clopentyl}acrylate (6)



The product was obtained as a colorless solid, yield 94%, m.p. 103-105 ºC. The ee (95%) was measured by HPLC using a chiral stationary phase [Daicel IC, n-heptane:EtOH = 9:1, 0.7 mL/min, t_R = 22.02 min (major), 11.94 min (minor)]. $[\alpha]_D^{22} = -60.3$ (c = 1.29, $CHCl_3$).

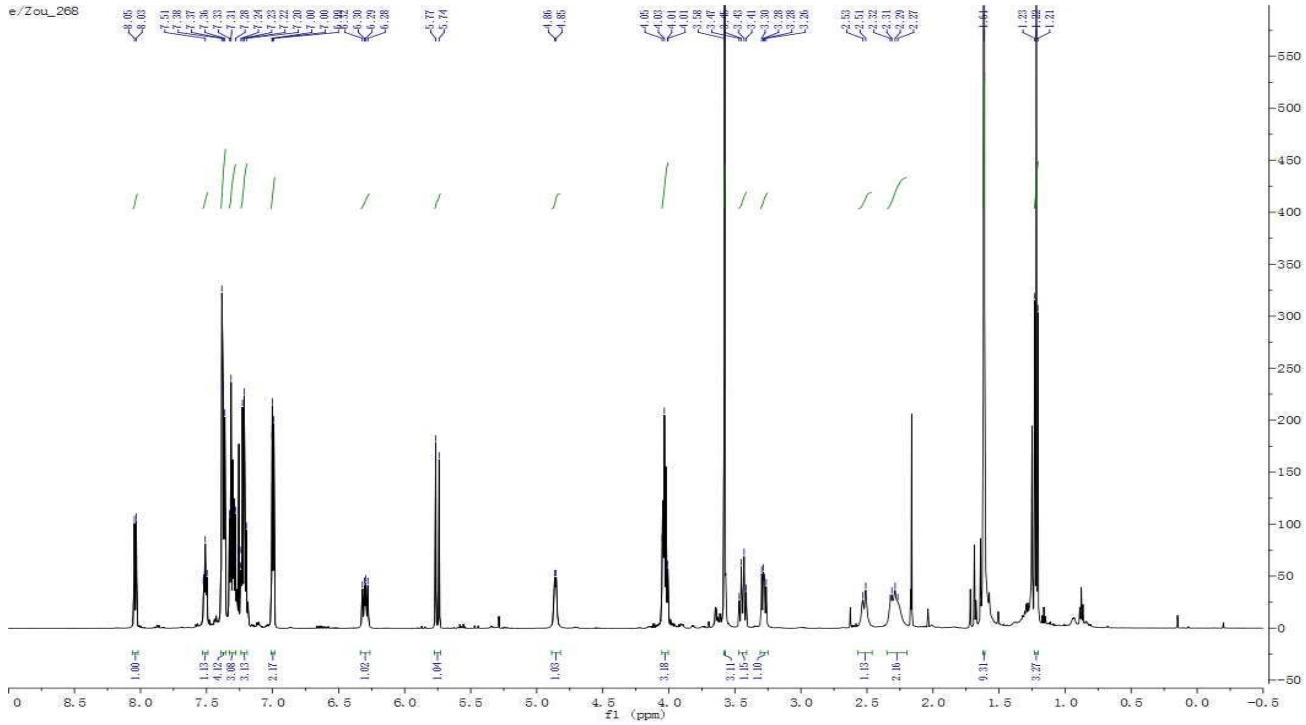
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.49 (bs, 1H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.40-7.37 (m, 2H), 7.31 (t, *J* = 7.1 Hz, 2H), 7.27 (t, *J* = 7.2 Hz, 1H), 7.24-7.19 (m, 4H), 7.04-7.01 (m, 3H), 6.40-6.36 (m, 1H), 5.78 (d, *J* = 15.6 Hz s, 1H), 4.87 (d, *J* = 7.3 Hz, 1H), 4.06-4.02 (m, 3H), 3.58 (s, 3H), 3.53-3.48 (m, 1H), 3.38-3.34 (m, 1H), 2.54 (d, *J* = 13.5 Hz, 1H), 2.37-2.32 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 178.0, 171.4, 166.0, 146.9, 141.2, 136.8, 133.3, 129.7, 129.3, 129.1, 128.8, 128.4, 128.3, 127.8, 127.4, 125.2, 124.0, 123.2, 111.1, 94.8, 60.7, 58.2, 54.9, 54.3, 51.5, 50.2, 42.1, 37.6, 29.7, 14.0. IR: 3287, 2935, 1716, 1552, 1469, 1217, 1029, 854, 747, 696. HRMS (ESI) calcd for $C_{41}H_{47}N_3O_9Na$: 591.2107; found: 591.2064.

5. References

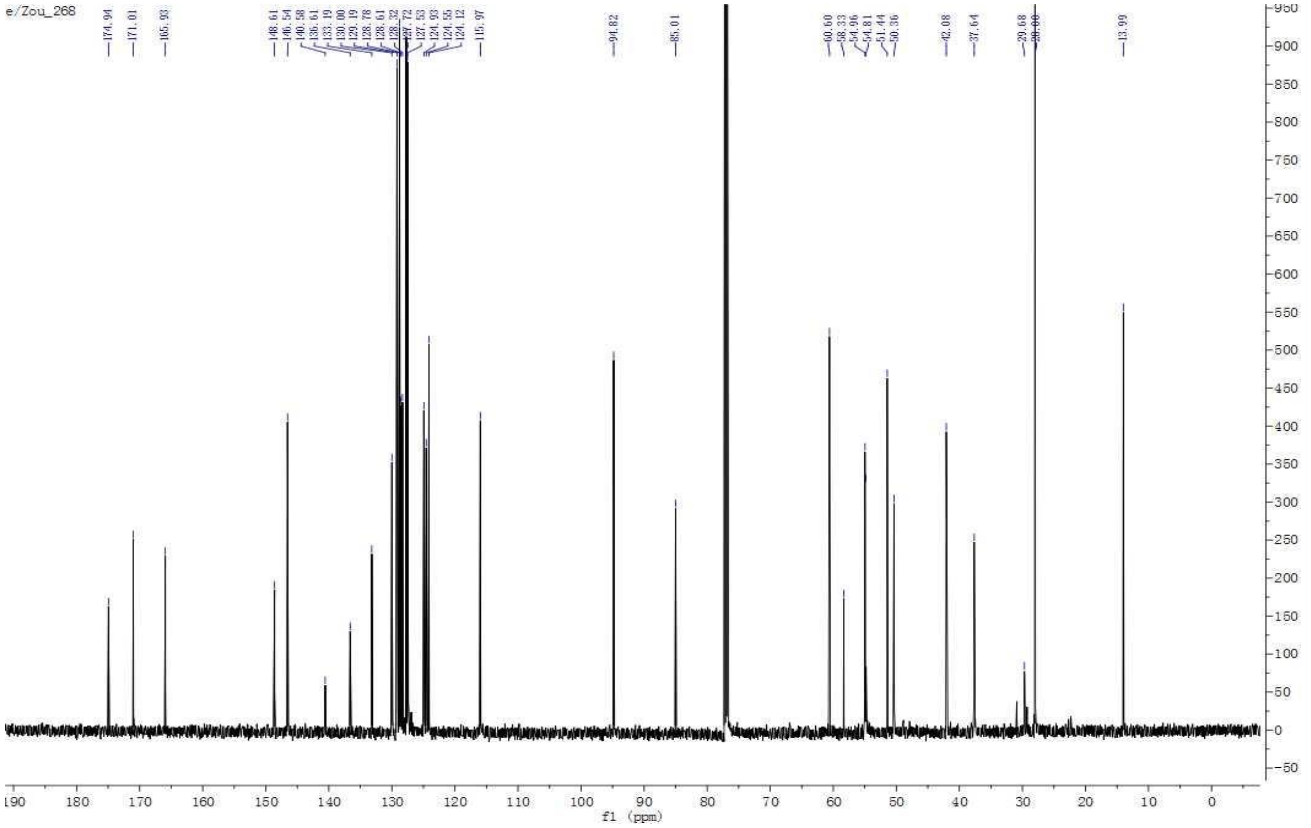
[1] M.-X. Zhao, Z.-W. Zhang, M.-X. Chen, W.-H. Tang, M. Shi, *Eur. J. Org. Chem*. **2001**, 3001-3008.
[2] S. Belot, A. Quintard, N. Krause, A. Alexakis, *Adv. Synth. Catal*. **2010**, *352*, 667-695.
[3] Q. Zhu, Y. Lu, *Angew. Chem.* **2010**, *122*, 7919-7922; *Angew. Chem. Int. Ed.* **2010**, *49*, 7753-7756.

6. NMR Spectra and HPLC Data

^{1}H NMR of **4a**



^{13}C NMR of **4a**



Chiral HPLC analysis: rac-**4a**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

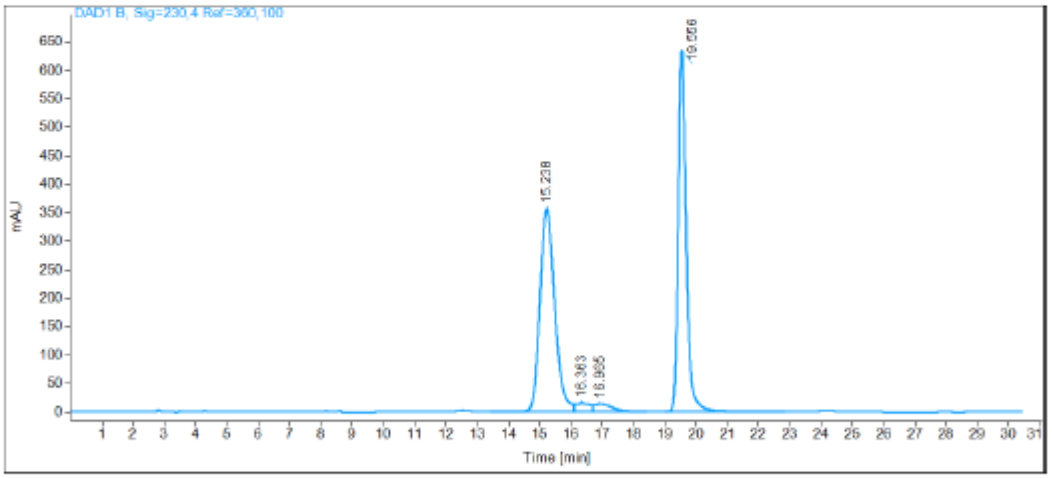
Sample name: Zou 91-2

Data file: C:\SNOOPY\ZOU\ZOU 91-2 IC.D
Description: Laufmittel: n-Heptan/EtOH 97:3 Die Probe ist DCM/EtOH/LM gelöst.

Injection date: 2/26/2014 9:25:46 AM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 22 bar **Start flow:** 0.700 ml/min **Column oven:** 30.01 °C



Name Zou 91-2

RT [min]	Type	Area%	Area	Height	Width [min]
15.24	BV	48.51	11654.49	355.90	0.50
16.36	VV	2.08	499.78	14.64	0.49
16.97	VB	2.27	546.02	13.29	0.61
19.56	BB	47.14	11325.64	634.99	0.27
	Sum	100.00	24025.93		

Chiral HPLC analysis: **4a**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

Sample name: Zou 267 TLC

Data file: C:\SNOOPY\ZOU\267TLCIC.D

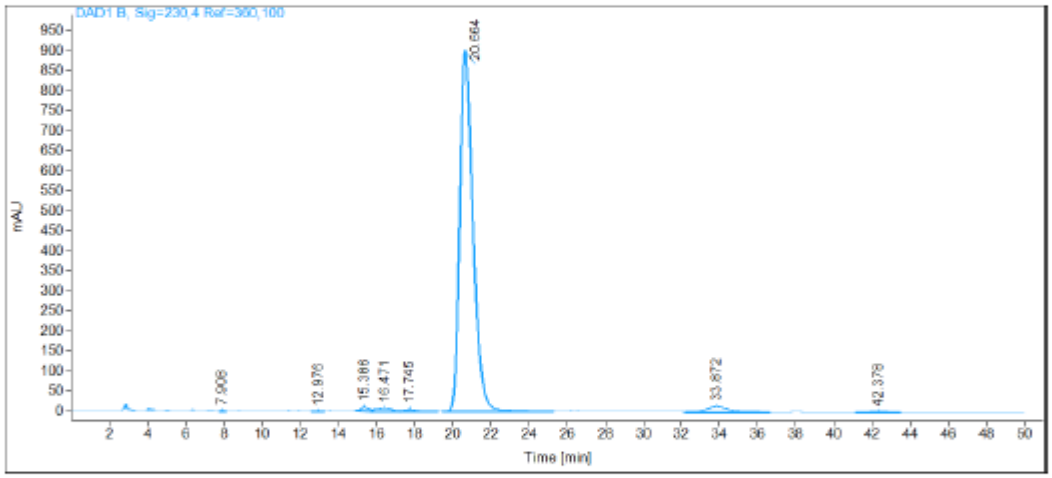
Description: Laufmittel: n-Heptan/EtOH 97:3;
Die Probe ist im LM/DCM gelöst.

Injection date: 6/16/2014 3:16:33 PM

Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

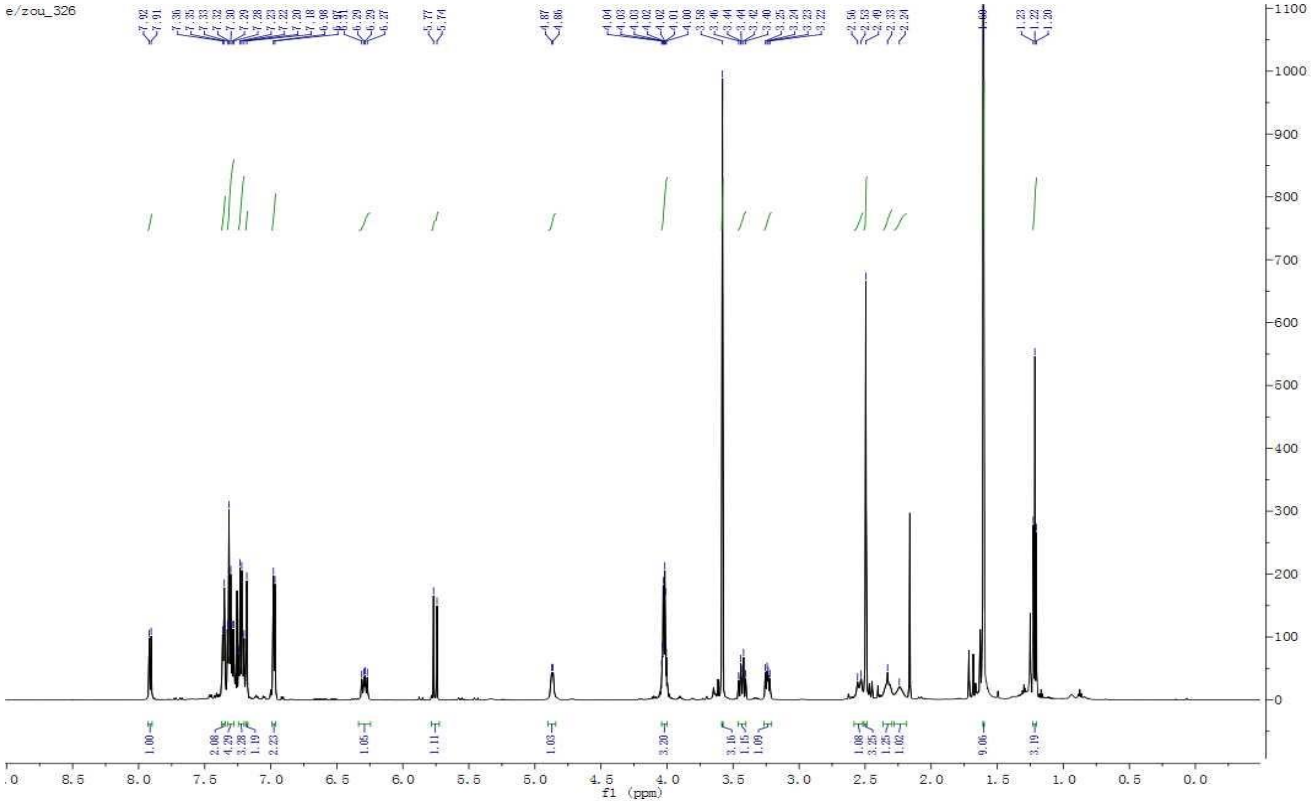
Pressure at start: 23 bar **Start flow:** 0.700 ml/min **Column oven:** 30 °C



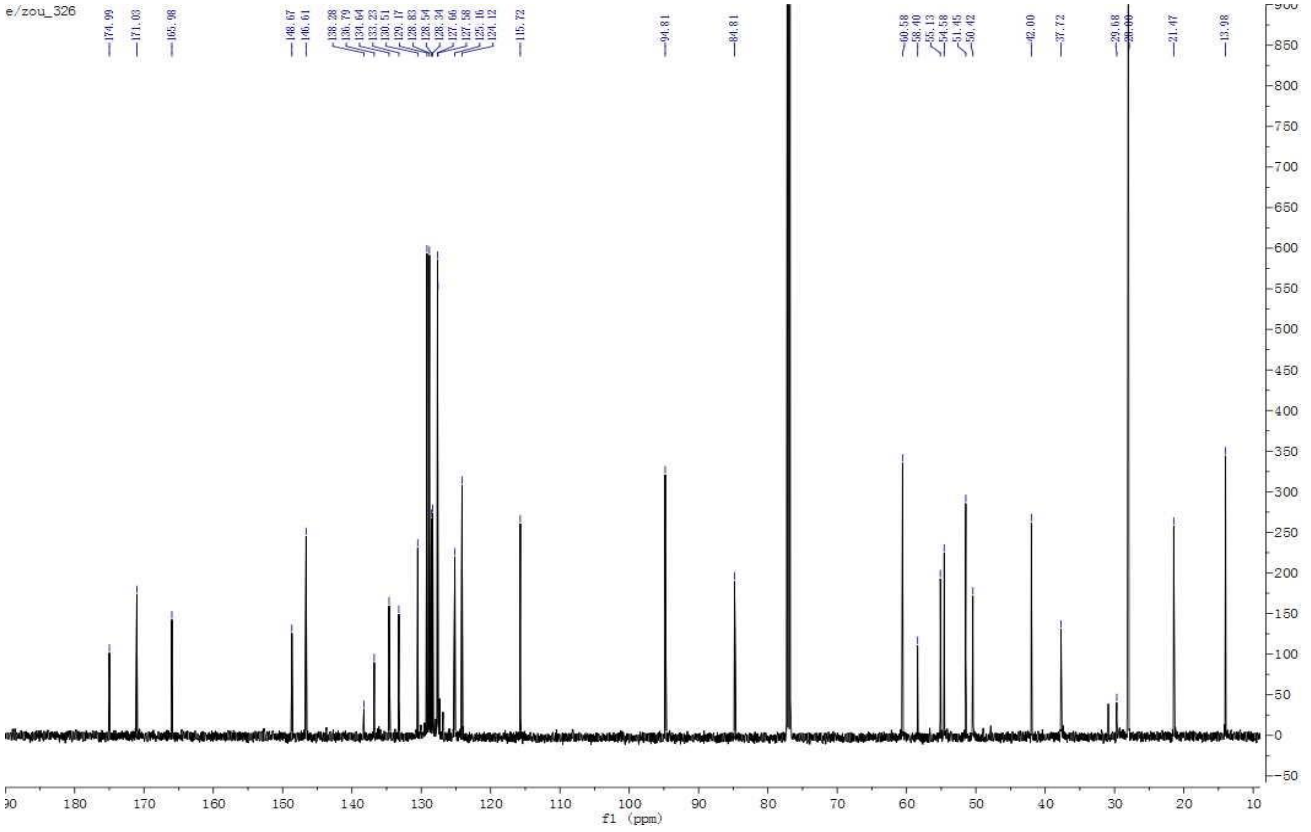
Name Zou 267 TLC

RT [min]	Type	Area%	Area	Height	Width [min]
7.91	BB	0.01	2.86	0.26	0.17
12.98	BB	0.01	6.15	0.30	0.32
15.39	BV	0.60	276.69	9.03	0.47
16.47	VV	0.99	454.73	8.77	0.75
17.74	VB	0.43	196.92	5.07	0.60
20.66	BB	95.60	43904.68	902.04	0.75
33.87	BB	2.23	1024.99	13.29	1.17
42.38	BB	0.12	56.38	0.91	0.75
	Sum	100.00	45923.40		

^{1}H NMR of **4b**



^{13}C NMR of **4b**



Chiral HPLC analysis: rac-**4b**

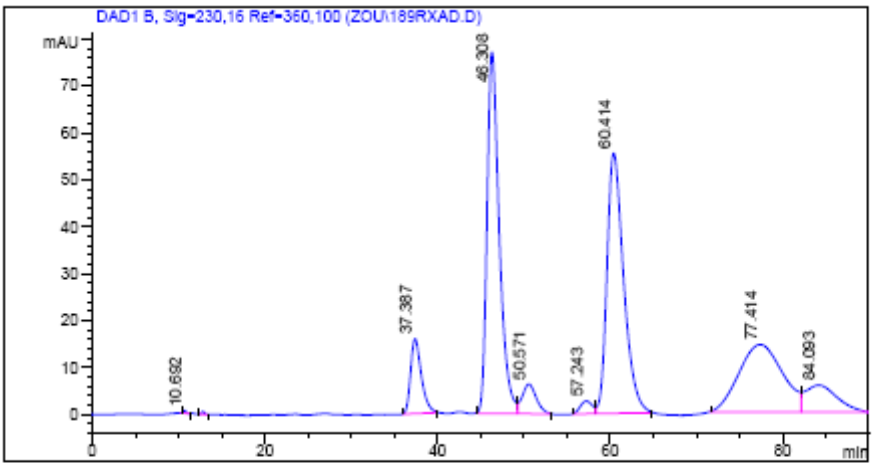
AK Enders - Analytische HPLC

Sample Name: Zou 189 neu
Data file: D:\GONZO\ZOU\189RXAD.D
Sample Info: Laufmittel: n-Heptan/IP 97:3
Die Probe ist in LM/DCM gelöst

Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 18:33:58
Injektion Date: 21.08.2014

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	4.3	4.6
Flow in ml/min:	0.30	0.30



‡	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	10.69	0.30	0.60	13.08	0.05
2	12.78	0.32	0.62	14.32	0.06
3	37.39	1.19	15.92	1378.61	5.76
4	46.31	1.45	76.97	7569.19	31.61
5	50.57	1.37	6.34	723.80	3.02
6	57.24	1.16	2.72	264.11	1.10
7	60.41	1.96	55.47	7445.76	31.10
8	77.41	4.12	14.39	5058.72	21.13
9	84.09	3.00	5.77	1475.01	6.16
Total				23942.62	100.00

Chiral HPLC analysis: **4b**

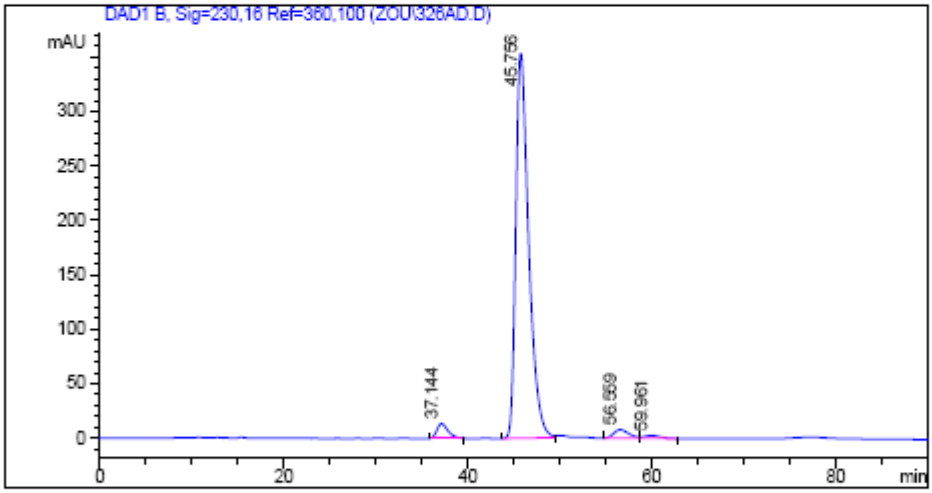
AK Enders - Analytische HPLC

Sample Name: Zou 326
Data file: D:\GONZO\ZOU\326AD.D
Sample Info: Laufmittel: n-Heptan/IP 97:3
Die Probe ist in LM/DCM gelöst

Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

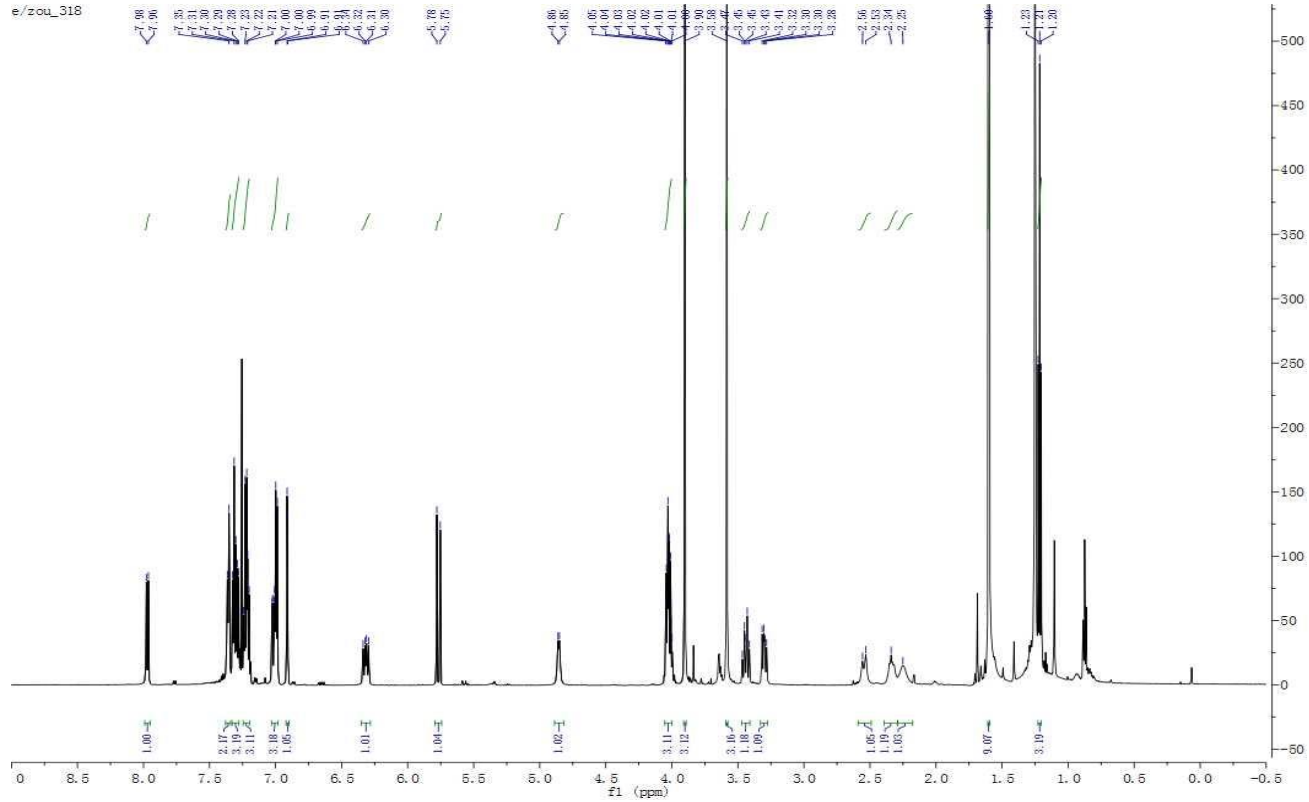
Injektion Time: 15:31:22
Injektion Date: 21.08.2014

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	4.3	4.7
Flow in ml/min:	0.30	0.30

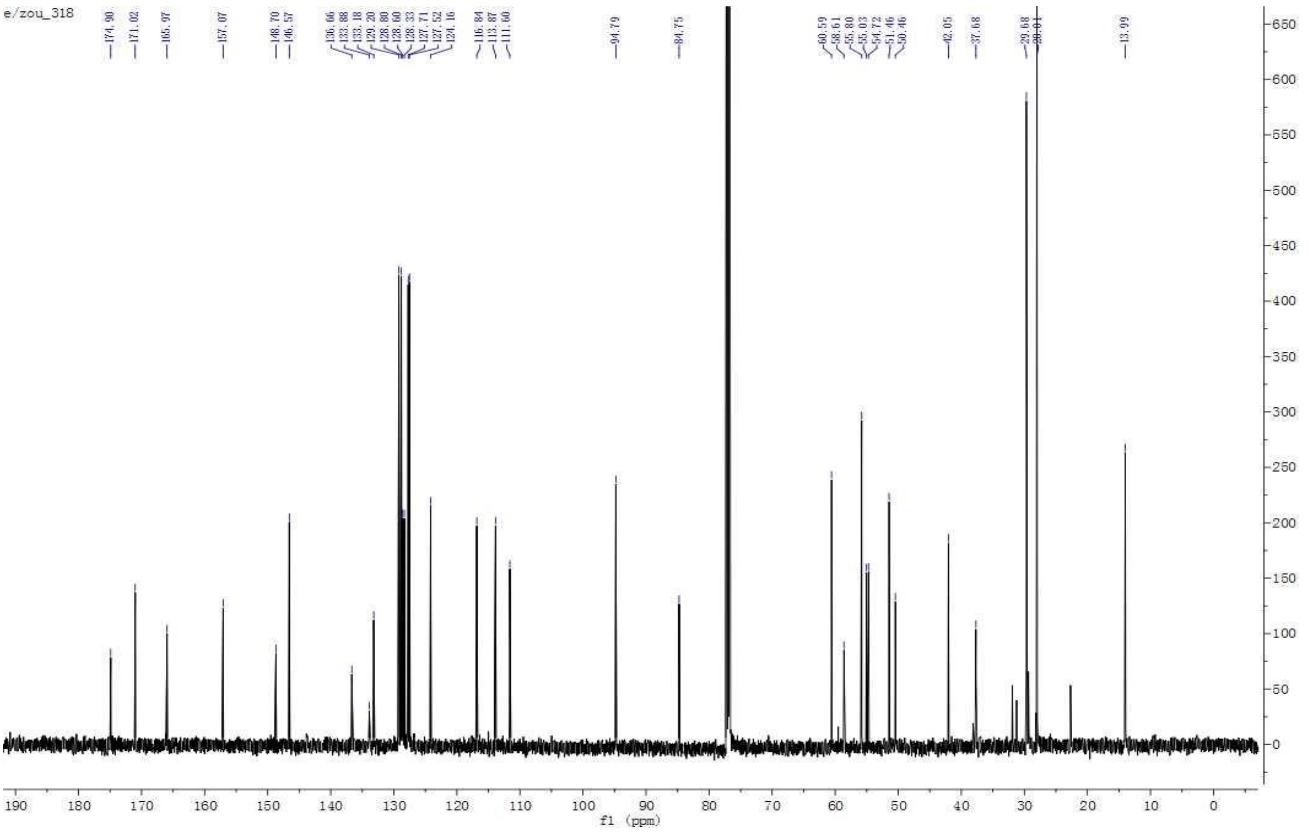


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	37.14	1.24	13.67	1175.15	3.19
2	45.76	1.44	353.50	34477.43	93.46
3	56.56	1.37	7.88	910.82	2.47
4	59.96	1.46	2.65	328.09	0.89
Total				36891.49	100.00

^{1}H NMR of **4c**



^{13}C NMR of **4c**



Chiral HPLC analysis: rac-**4c**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

Sample name: Zou 344 rac

Data file: C:\SNOOPY\ZOU\344RIA.D

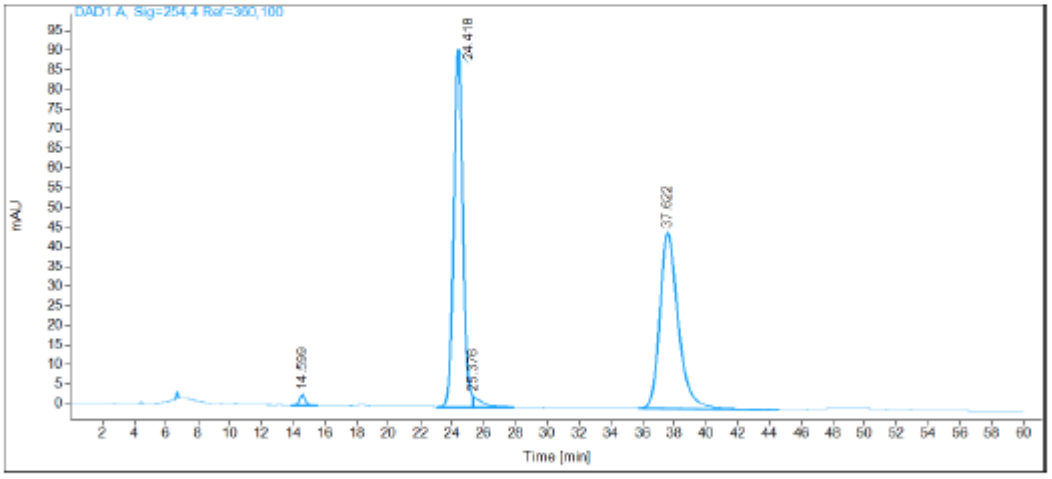
Description: Laufmittel: n-Heptan/IP 95:5; Probe ist in LM/DCM gelöst.

Injection date: 8/28/2014 5:28:02 PM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 33 bar **Start flow:** 0.700 ml/min **Column oven:** 30 °C



Name Zou 344 rac

RT [min]	Type	Area%	Area	Height	Width [min]
14.60	BB	0.88	65.10	2.50	0.40
24.42	MF	48.96	3636.45	91.15	0.66
25.38	FM	1.32	98.23	2.57	0.64
37.62	BB	48.84	3627.65	44.74	1.23
	Sum	100.00	7427.43		

Chiral HPLC analysis: **4c**

AK Prof. Enders - Analytiklabor 4.04

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Sample name: Zou 318

Data file: C:\SNOOPY\ZOU\318IA.D

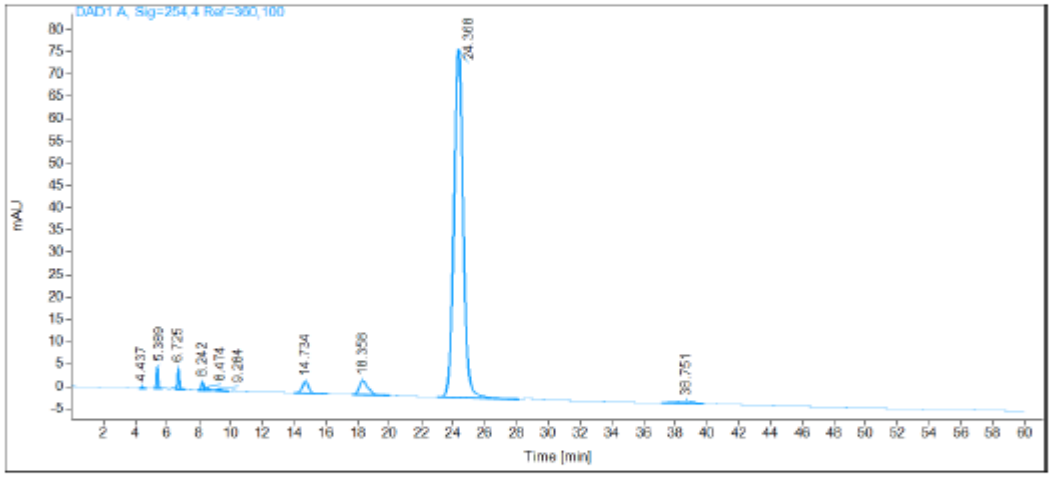
Description: Laufmittel: n-Heptan/IP 95:5; Probe ist in LM/DCM gelöst.

Injection date: 9/1/2014 4:16:44 PM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

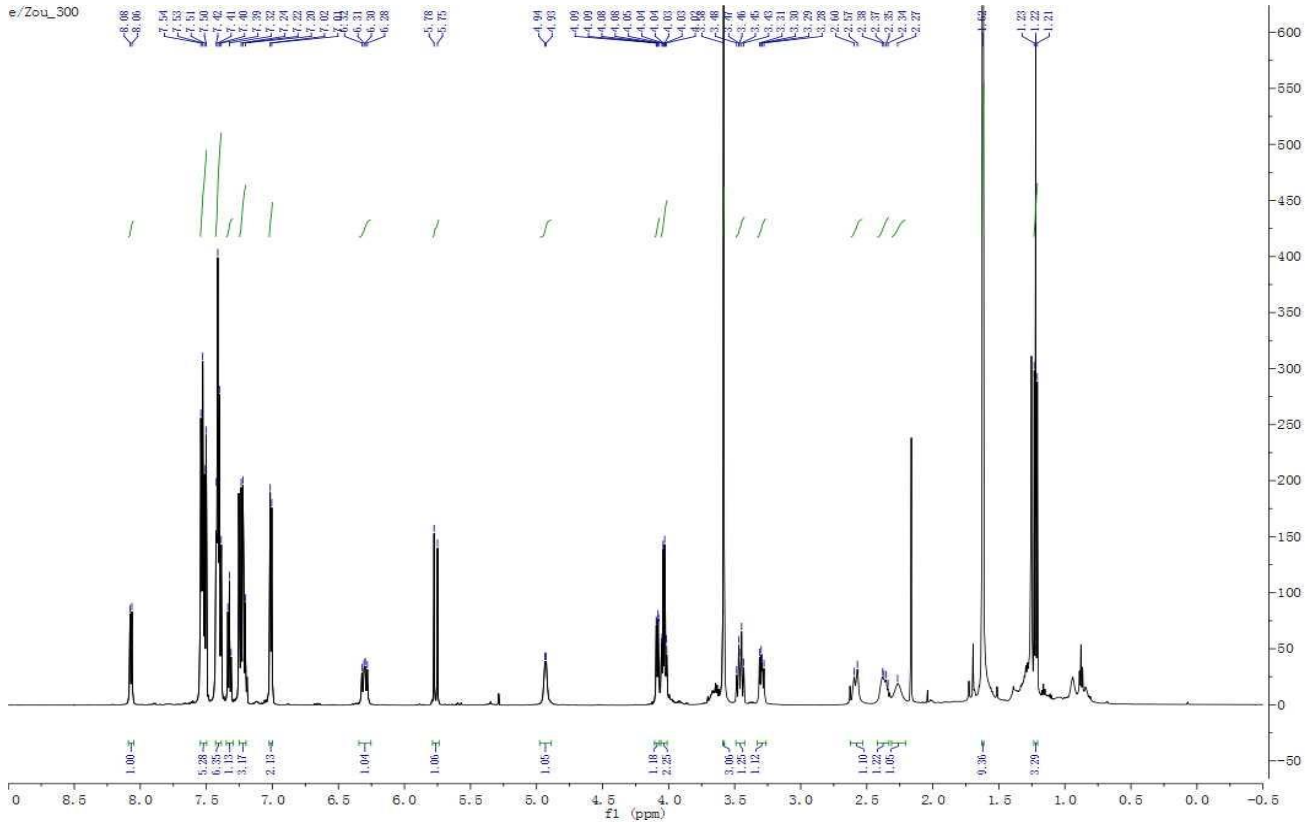
Pressure at start: 32 bar **Start flow:** 0.700 ml/min **Column oven:** 29.99 °C



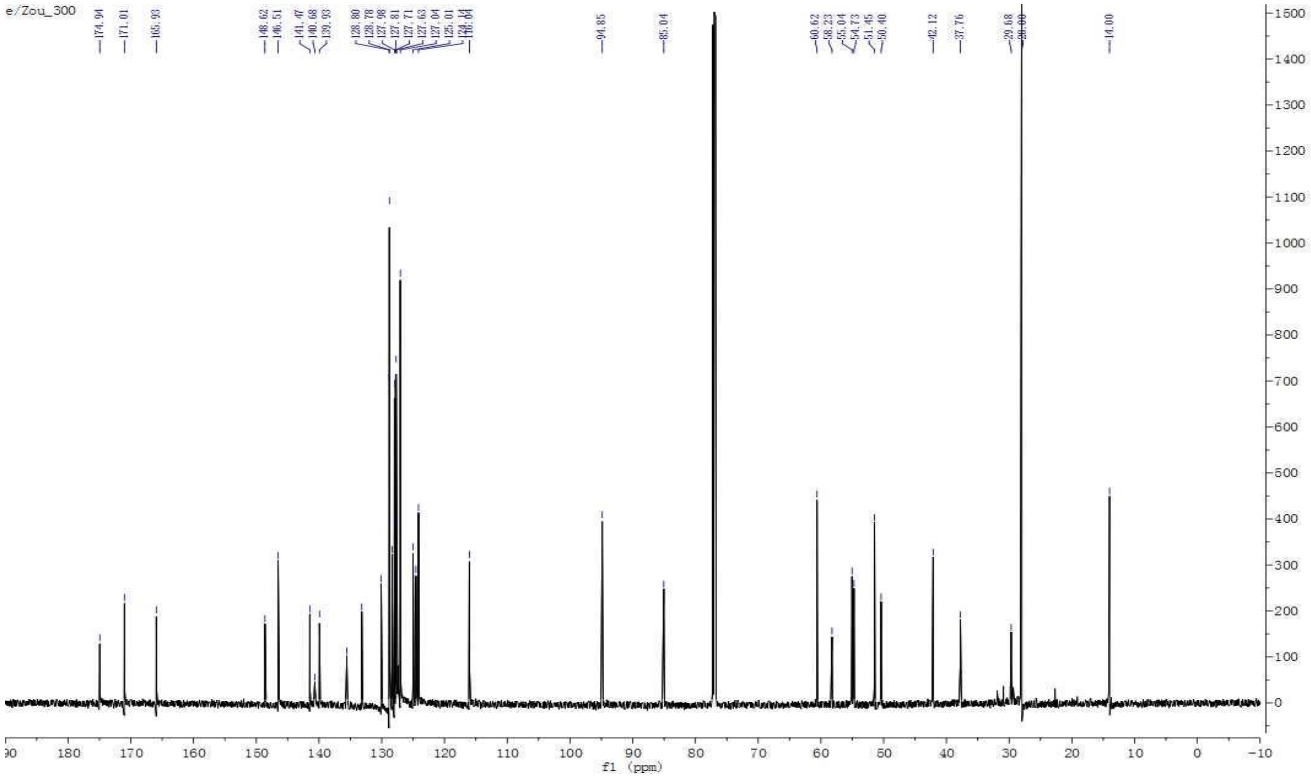
Name Zou 318

RT [min]	Type	Area%	Area	Height	Width [min]
4.44	BV	0.10	3.69	0.42	0.13
5.39	VV	1.07	37.86	4.81	0.12
6.72	VB	1.09	38.53	4.73	0.12
8.24	BV	0.48	17.03	1.74	0.15
8.47	VB	0.29	10.06	0.74	0.20
9.28	BB	0.19	6.61	0.40	0.25
14.73	BB	2.15	75.78	2.68	0.42
18.36	VB	3.51	123.99	3.16	0.57
24.37	BB	89.90	3171.61	78.09	0.62
38.75	MM	1.22	42.91	0.50	1.42
	Sum	100.00	3528.06		

^{1}H NMR of **4d**



^{13}C NMR of **4d**



Chiral HPLC analysis: rac-**4d**

AK Enders - Analytische HPLC

Sample Name: Zou 299 rac
Data file: D:\BERT\ZOU\299RW.D
Sample Info: Laufmittel: n-Heptan/EtOH 7:3;
Die Probe ist in DCM/LM gelöst

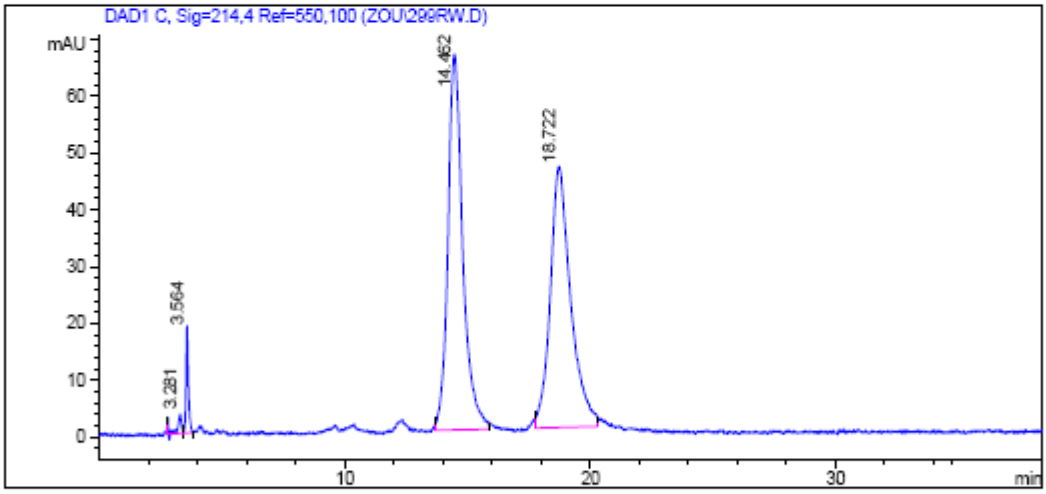
Agilent Technologies

Säule: WHELK.M
Säuleninfo: (s,s)-Whelk O1 (250x4,6)mm

Operator: Analytik Labor AKEN

Injektion Time: 14:44:44
Injektion Date: 10.07.2014

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	47.4	47.4
Flow in ml/min:	0.7	0.7



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.28	0.17	3.35	39.21	0.70
2	3.56	0.10	18.25	121.55	2.17
3	14.46	0.62	66.09	2780.72	49.70
4	18.72	0.80	45.91	2653.62	47.43
Total				5595.11	100.00

Chiral HPLC analysis: **4d**

AK Enders - Analytische HPLC

Agilent Technologies

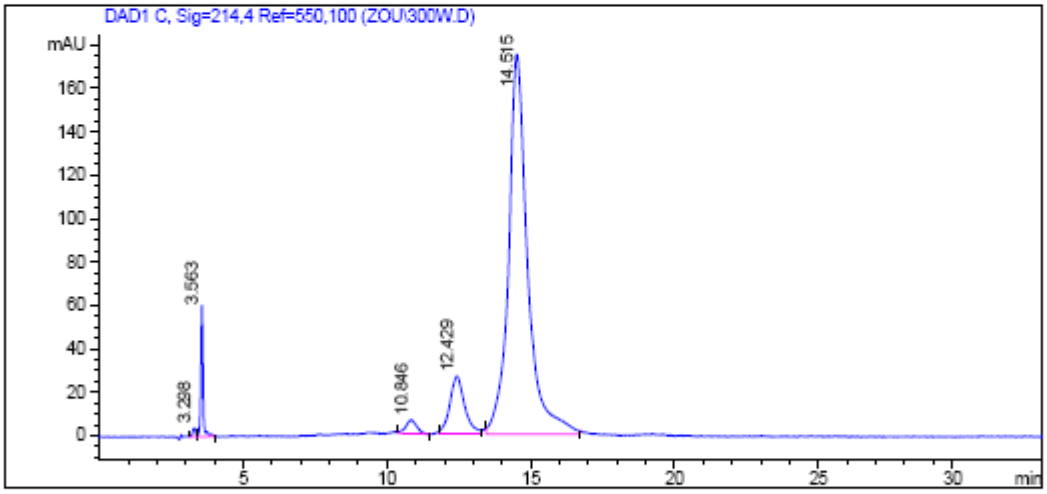
Sample Name: Zou 300
Data file: D:\BERT\ZOU\300W.D
Sample Info: Laufmittel: n-Heptan/EtOH 7:3;
Die Probe ist in DCM/LM gelöst

Säule: WHELK.M
Säuleninfo: (s,s)-Whelk O1 (250x4,6)mm

Operator: Analytik Labor AKEN

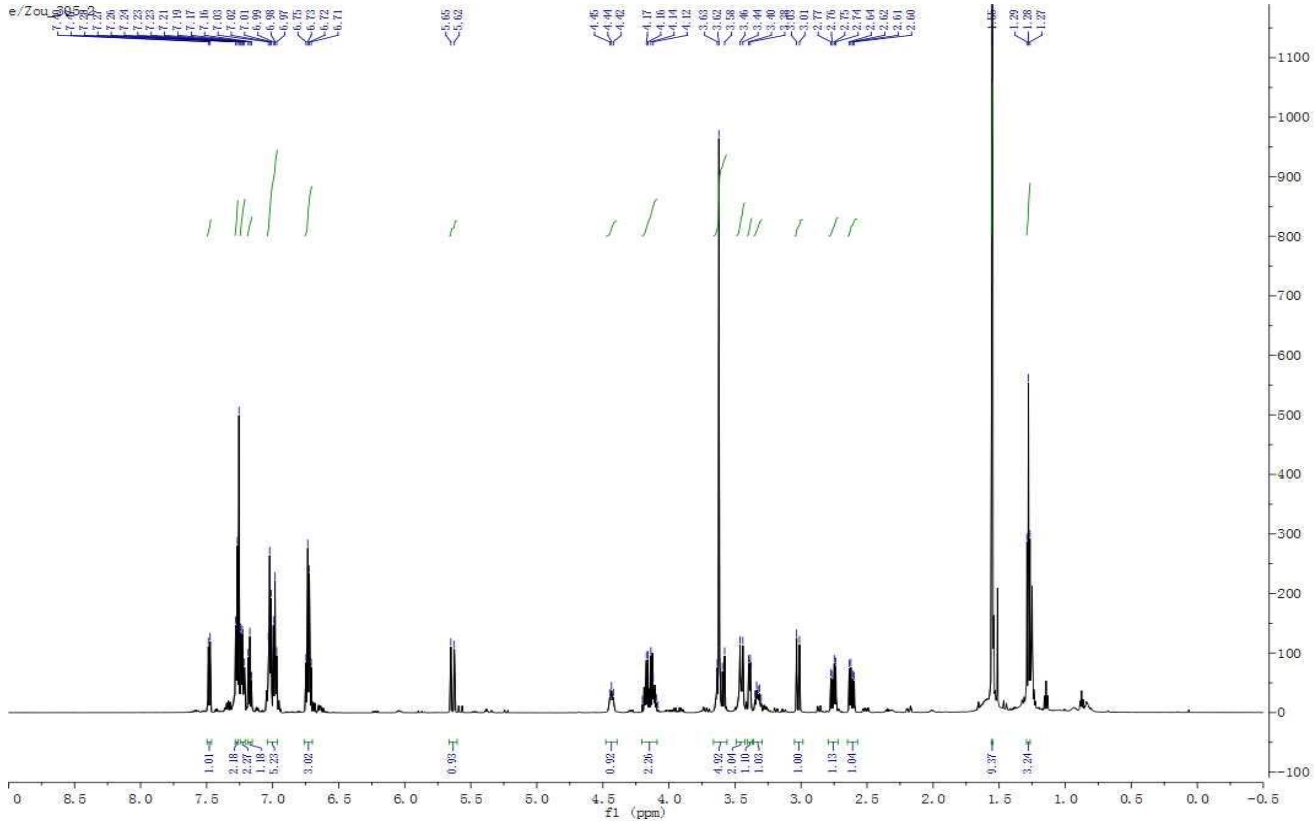
Injektion Time: 15:01:54
Injektion Date: 14.07.2014

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	47.2	47.6
Flow in ml/min:	0.7	0.7

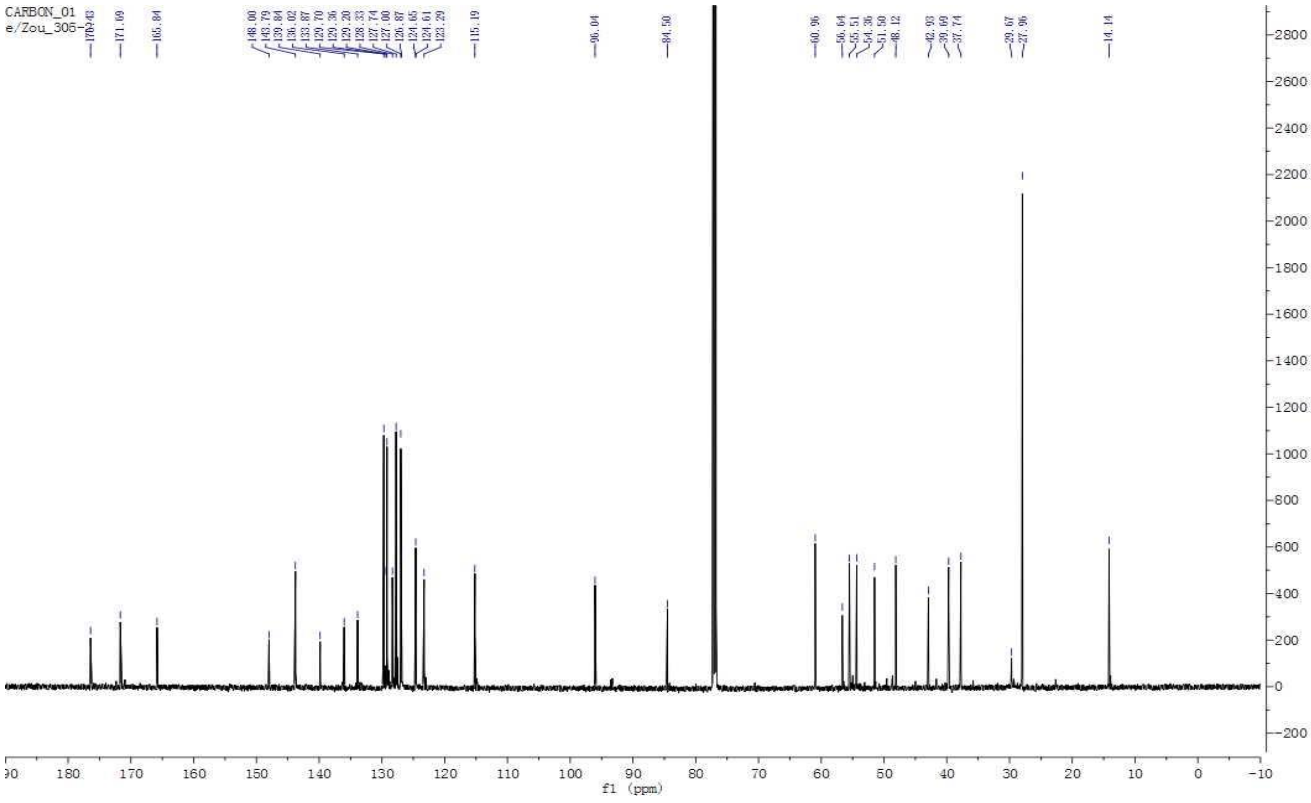


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.30	0.12	3.86	30.45	0.32
2	3.56	0.09	58.69	330.51	3.44
3	10.85	0.40	6.39	171.00	1.78
4	12.43	0.52	26.66	968.36	10.08
5	14.51	0.67	175.10	8102.05	84.38
Total				9602.37	100.00

^{1}H NMR of **4e**



^{13}C NMR of **4e**



Chiral HPLC analysis: rac-**4e**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

Sample name: Zou 356 + 349 T

Data file: C:\SNOOPY\ZOU\ZOU 356 + 349 T IA.D

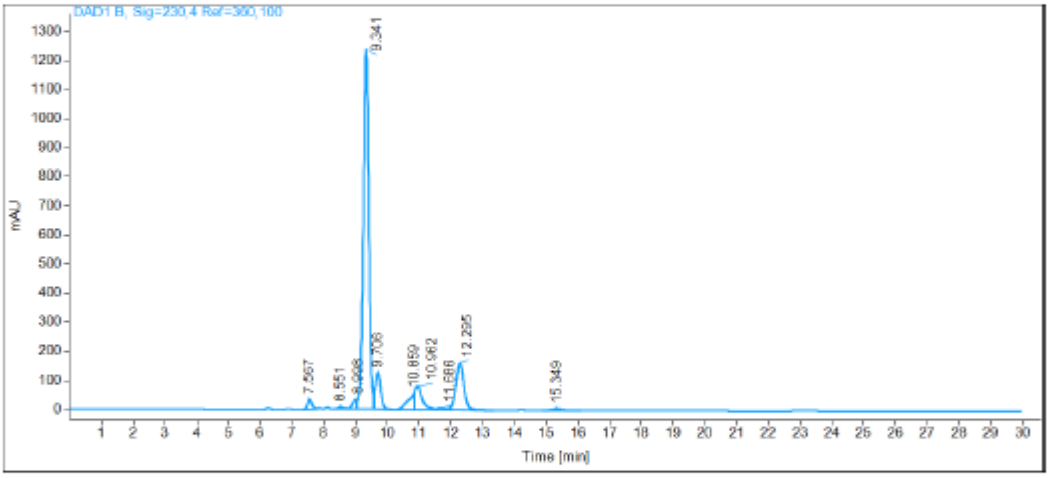
Description: Laufmittel: n-Heptan/EtOH 7:3 Die Probe ist DCM/LM gelöst.

Injection date: 9/15/2014 2:03:59 PM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 30 bar **Start flow:** 0.500 ml/min **Column oven:** 29.99 °C



Name Zou 356 + 349 T

RT [min]	Type	Area%	Area	Height	Width [min]
7.57	BV	1.47	324.54	32.92	0.15
8.55	BB	0.35	78.16	6.95	0.17
9.00	BV	1.25	276.37	30.35	0.14
9.34	VV	66.09	14582.02	1235.90	0.18
9.71	VB	7.04	1554.16	125.07	0.19
10.86	MF	3.52	776.32	59.00	0.22
10.96	FM	5.94	1311.59	81.93	0.27
11.69	VV	0.45	98.51	5.84	0.25
12.30	VB	13.25	2923.73	162.50	0.28
15.35	BB	0.63	138.36	6.14	0.35
	Sum	100.00	22063.76		

Chiral HPLC analysis: **4e**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

Sample name: Zou 356

Data file: C:\SNOOPY\ZOU\356IA.D

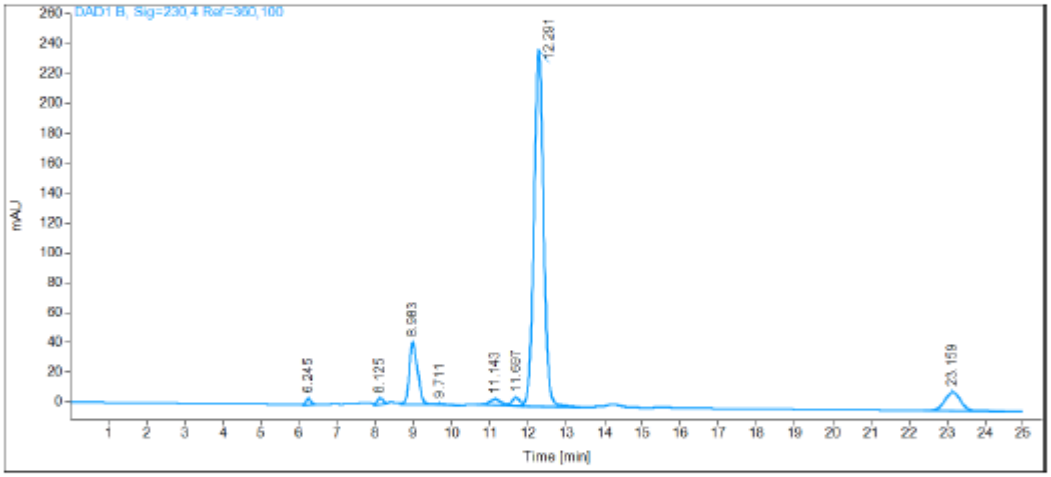
Description: Laufmittel: n-Heptan/EtOH 7:3; Probe ist in LM/DCM gelöst.

Injection date: 9/15/2014 12:19:06 PM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

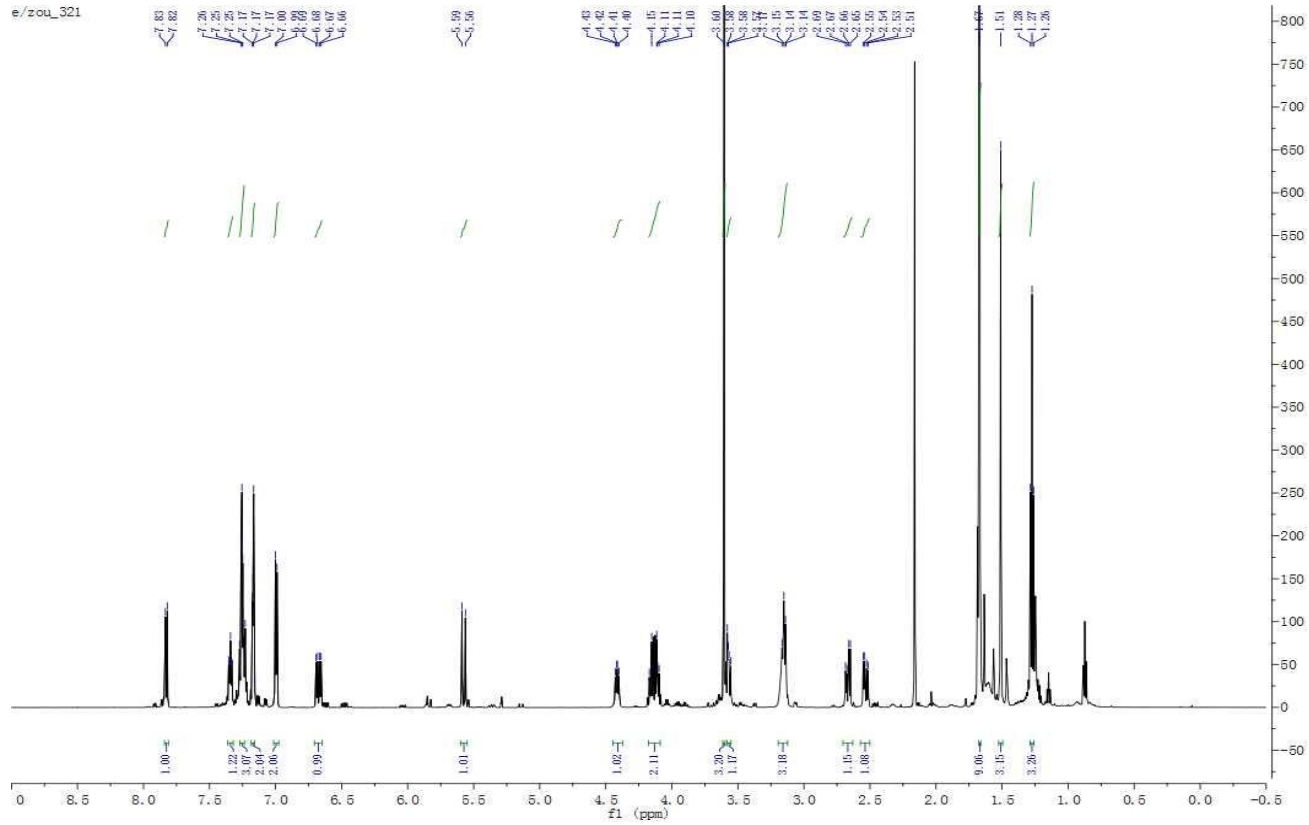
Pressure at start: 30 bar **Start flow:** 0.500 ml/min **Column oven:** 30.01 °C



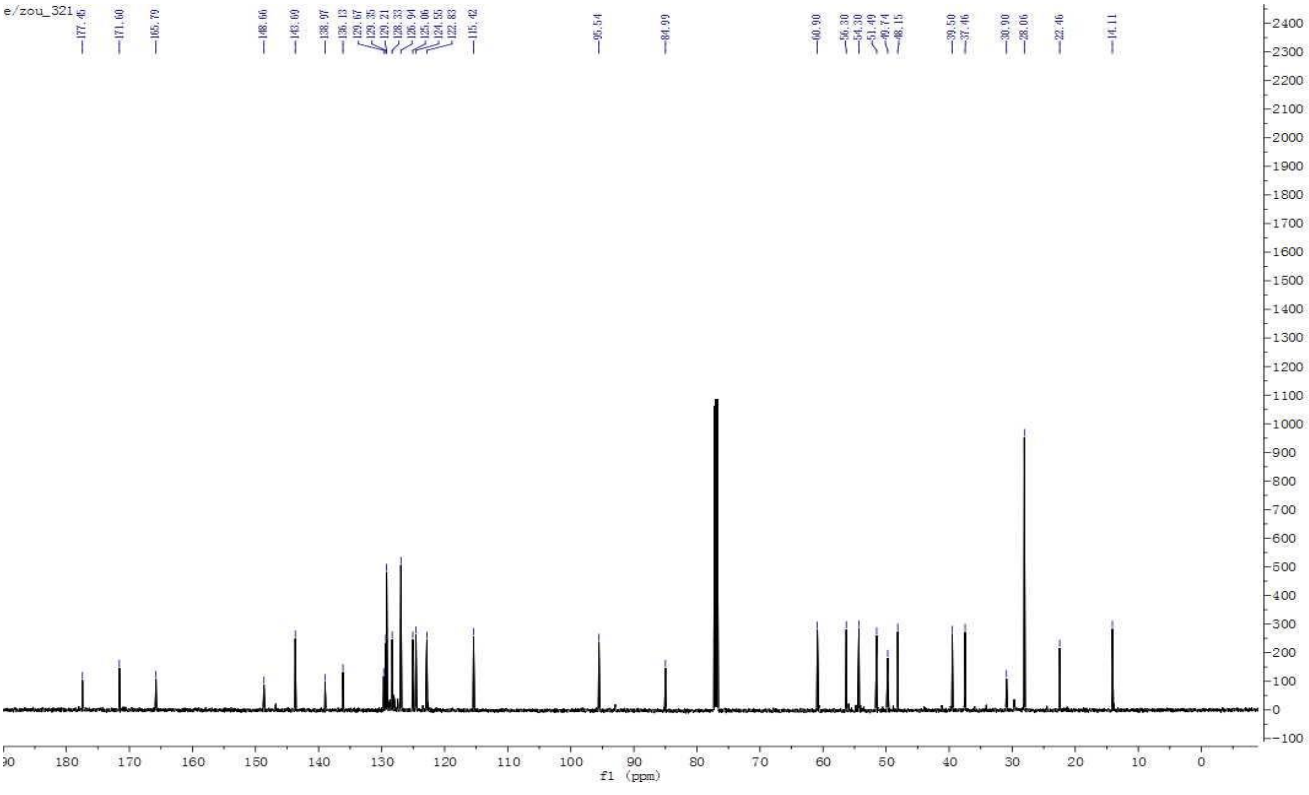
Name Zou 356

RT [min]	Type	Area%	Area	Height	Width [min]
6.25	MM	0.79	43.70	4.30	0.17
8.13	MM	0.89	48.78	4.25	0.19
8.98	VV	11.51	632.99	41.36	0.22
9.71	VB	0.32	17.60	0.96	0.27
11.14	BV	1.64	90.07	3.81	0.36
11.70	VV	1.44	79.25	5.30	0.23
12.29	VB	76.79	4223.29	238.83	0.27
23.16	BBA	6.62	364.28	12.53	0.45
	Sum	100.00	5499.96		

^{1}H NMR of **4f**



^{13}C NMR of **4f**



Chiral HPLC analysis: rac-**4f**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

Sample name: Zou 190 rac

Data file: C:\SNOOPY\ZOU\190RXIA.D

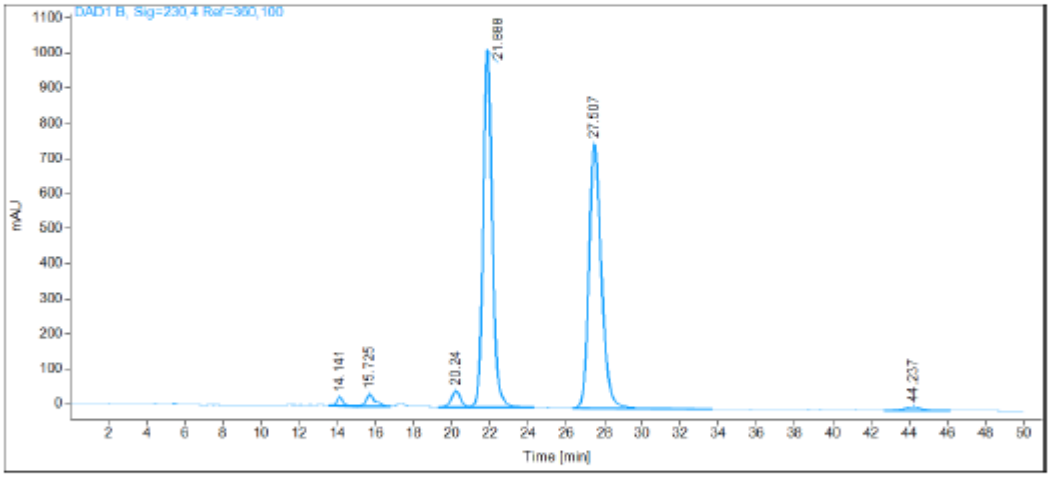
Description: Laufmittel: n-Heptan/IP 95:5;
Probe ist in LM/DCM gelöst.

Injection date: 8/21/2014 11:55:37 AM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 32 bar **Start flow:** 0.700 ml/min **Column oven:** 29.98 °C



Name Zou 190 rac

RT [min]	Type	Area%	Area	Height	Width [min]
14.14	BV	0.80	573.74	23.76	0.36
15.73	VV	1.51	1089.98	33.25	0.47
20.24	BV	2.08	1501.04	46.64	0.50
21.89	VV	47.61	34315.27	1018.71	0.51
27.51	VB	47.00	33875.26	752.95	0.68
44.24	VB	1.00	719.29	10.13	1.08
	Sum	100.00	72074.58		

Chiral HPLC analysis: **4f**

AK Prof. Enders - Analytiklabor 4.04

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Sample name: Zou 321 down

Data file: C:\SNOOPY\ZOU\321DO\A.D

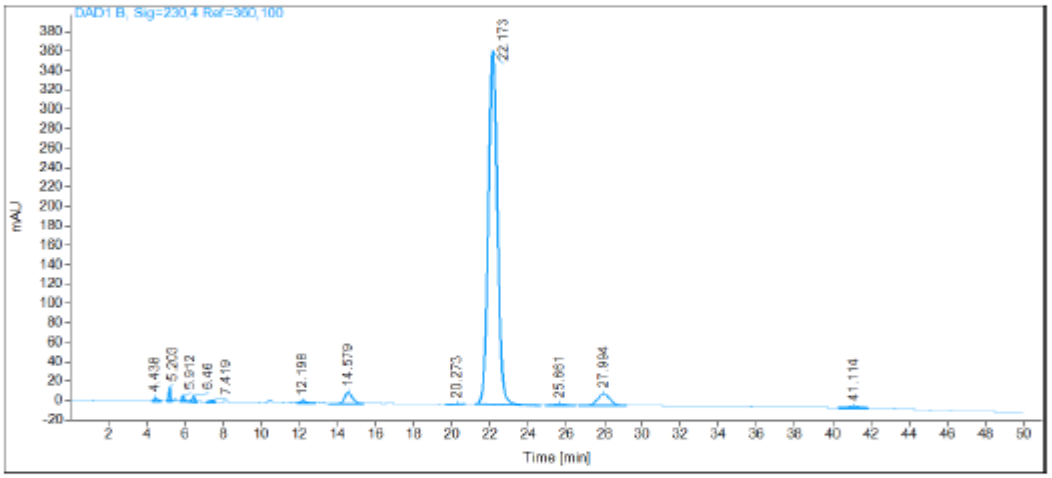
Description: Laufmittel: n-Heptan/IP 95:5;
Probe ist in LM/DCM gelöst.

Injection date: 8/21/2014 1:47:51 PM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

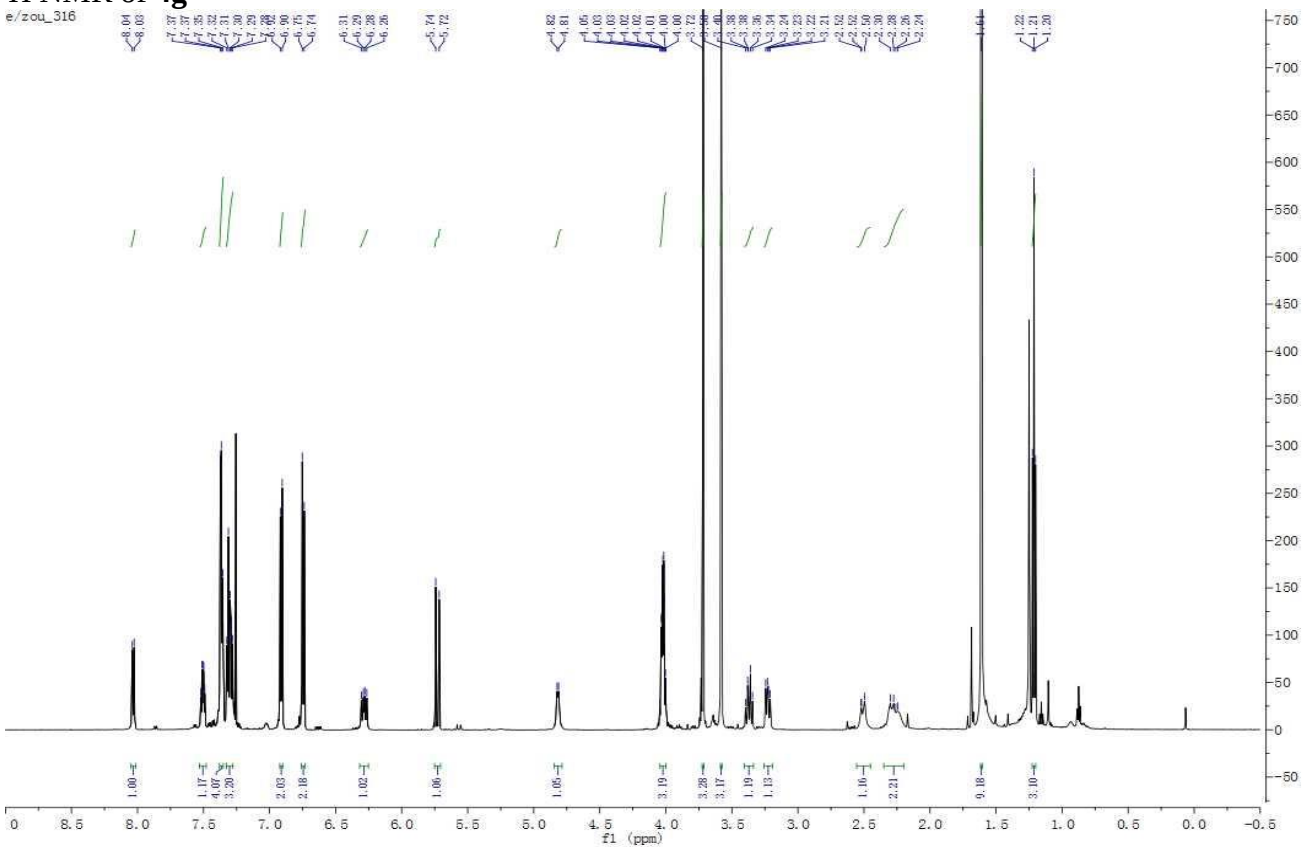
Pressure at start: 32 bar **Start flow:** 0.700 ml/min **Column oven:** 30.01 °C



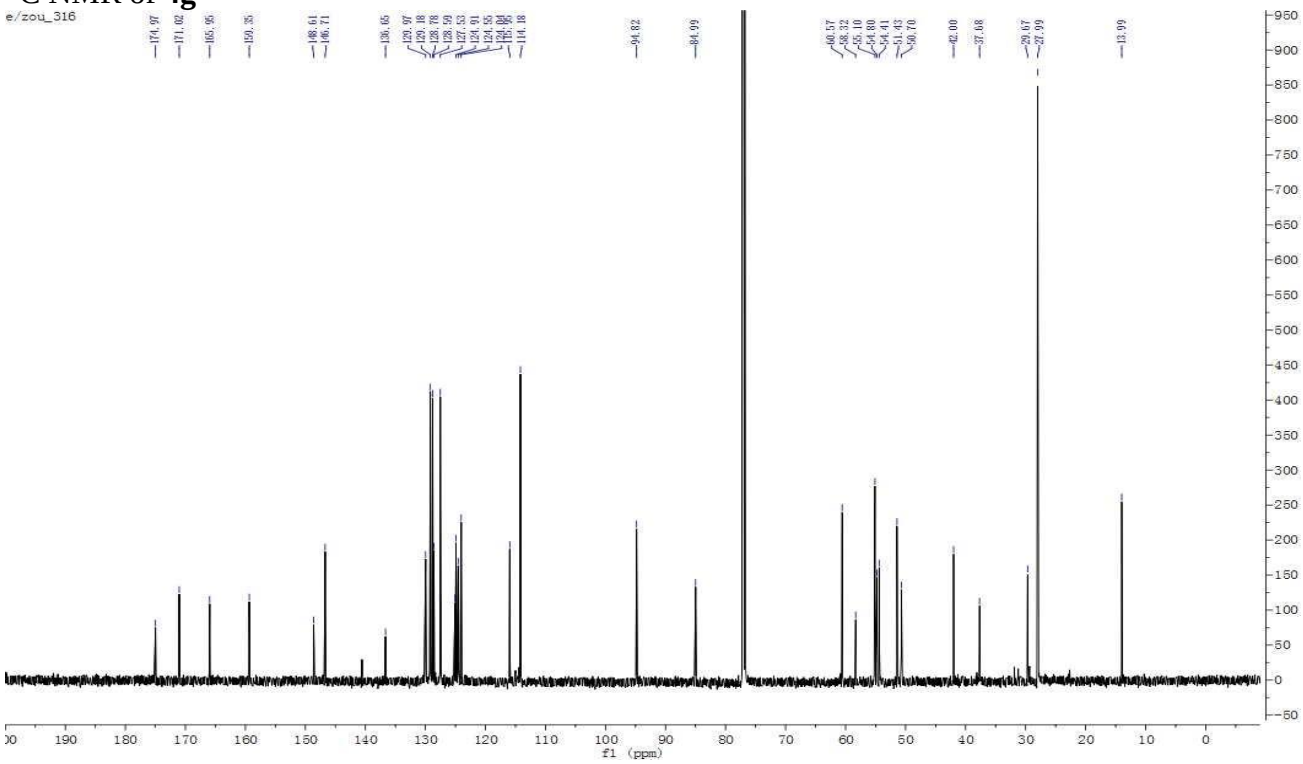
Name Zou 321 down

RT [min]	Type	Area%	Area	Height	Width [min]
4.44	VV	0.36	48.63	4.16	0.16
5.20	VB	0.65	86.57	14.77	0.09
5.91	BV	0.33	44.74	6.57	0.11
6.46	VV	0.43	57.67	6.30	0.13
7.42	BV	0.18	24.20	1.98	0.18
12.20	VB	0.39	52.77	1.89	0.41
14.58	BV	2.50	334.89	11.86	0.42
20.27	BB	0.16	21.64	0.73	0.48
22.17	BB	89.70	12034.51	364.83	0.51
25.66	BB	0.58	78.36	2.03	0.59
27.99	BB	4.03	540.81	12.05	0.69
41.11	MM	0.68	91.71	1.62	0.94
	Sum	100.00	13416.51		

^{1}H NMR of **4g**



^{13}C NMR of **4g**



Chiral HPLC analysis: rac-**4g**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

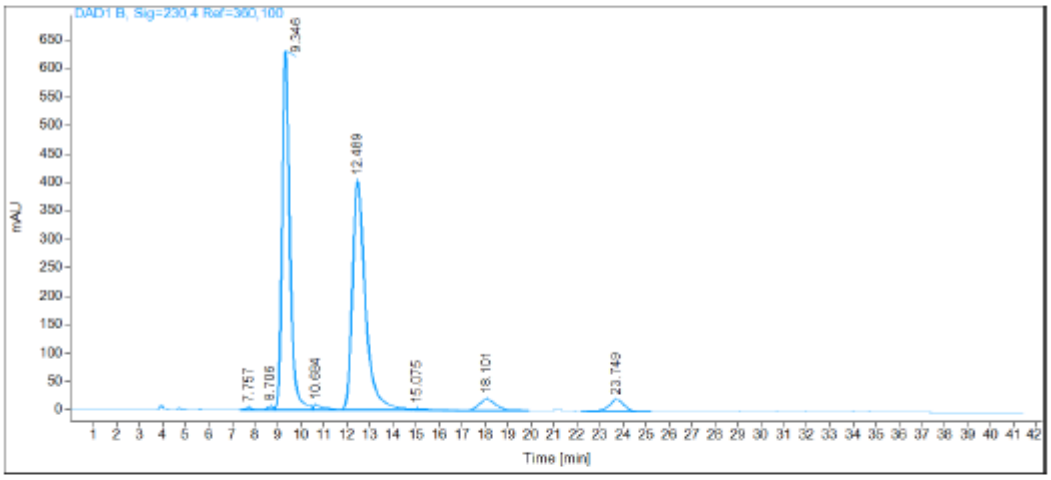
Sample name: Zou 262 rac

Data file: C:\SNOOPY\ZOU\ZOU 262 RAC ZIC.D
Description: Laufmittel: n-Heptan/IP 7:3 Die Probe ist DCM/LM gelöst.

Injection date: 7/9/2014 11:35:31 AM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 23 bar **Start flow:** 0.500 ml/min **Column oven:** 30 °C



Name Zou 262 rac

RT [min]	Type	Area%	Area	Height	Width [min]
7.76	VB	0.24	81.29	3.66	0.33
8.71	BV	0.33	108.54	5.87	0.28
9.35	VV	44.93	14975.37	630.27	0.36
10.68	VB	0.68	227.48	7.03	0.45
12.49	BV	47.69	15894.60	401.00	0.60
15.07	VB	0.41	137.93	2.61	0.75
18.10	BV	3.01	1004.52	18.92	0.81
23.75	BB	2.70	899.71	19.90	0.68
	Sum	100.00	33329.45		

Chiral HPLC analysis: **4g**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

Sample name: Zou 325 TLC

Data file: C:\SNOOPY\ZOU\325TLCIC.D

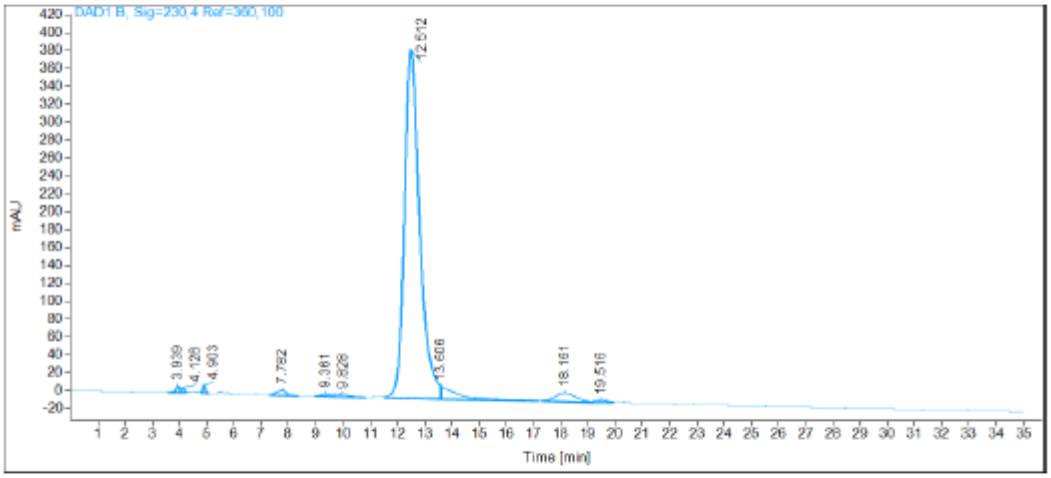
Description: Laufmittel: n-Heptan/IP 7:3;
Probe ist in LM/DCM gelöst.

Injection date: 8/25/2014 9:10:20 AM

Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

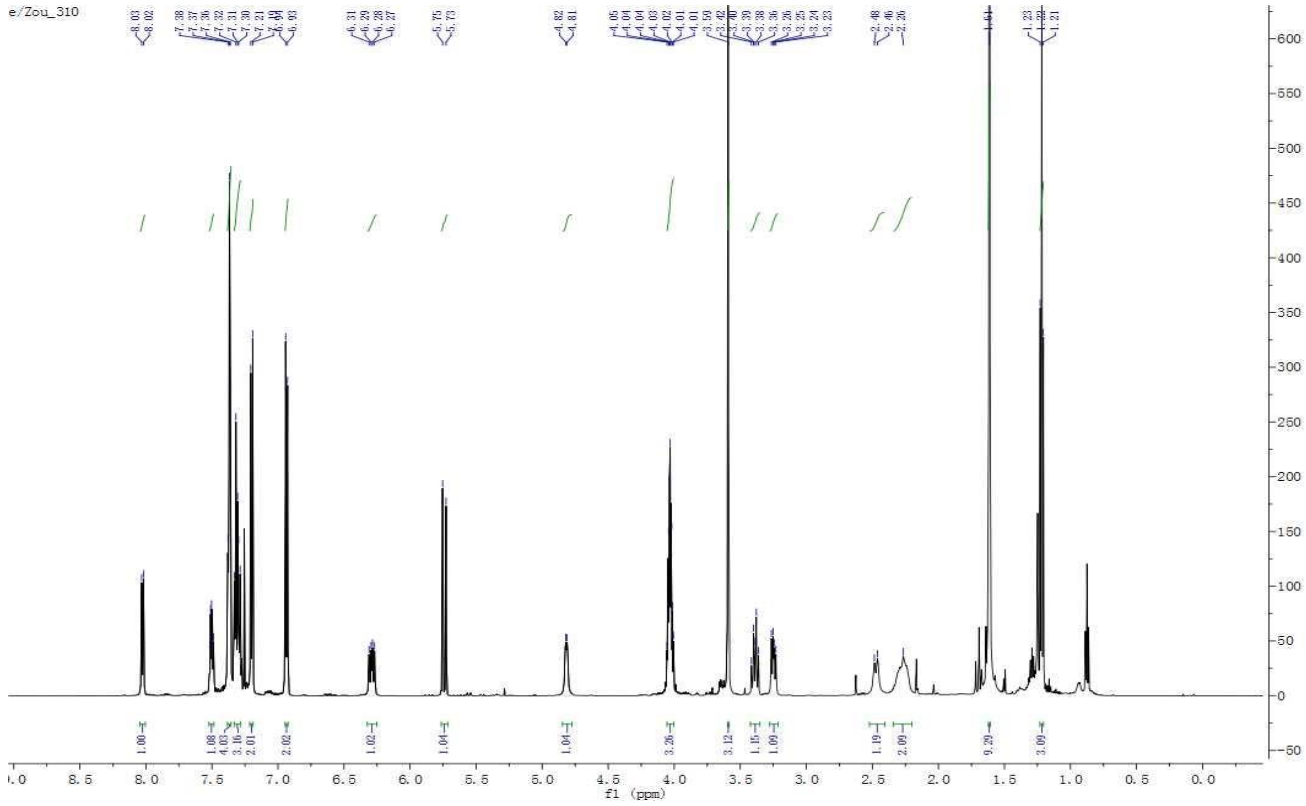
Pressure at start: 26 bar **Start flow:** 0.500 ml/min **Column oven:** 29.99 °C



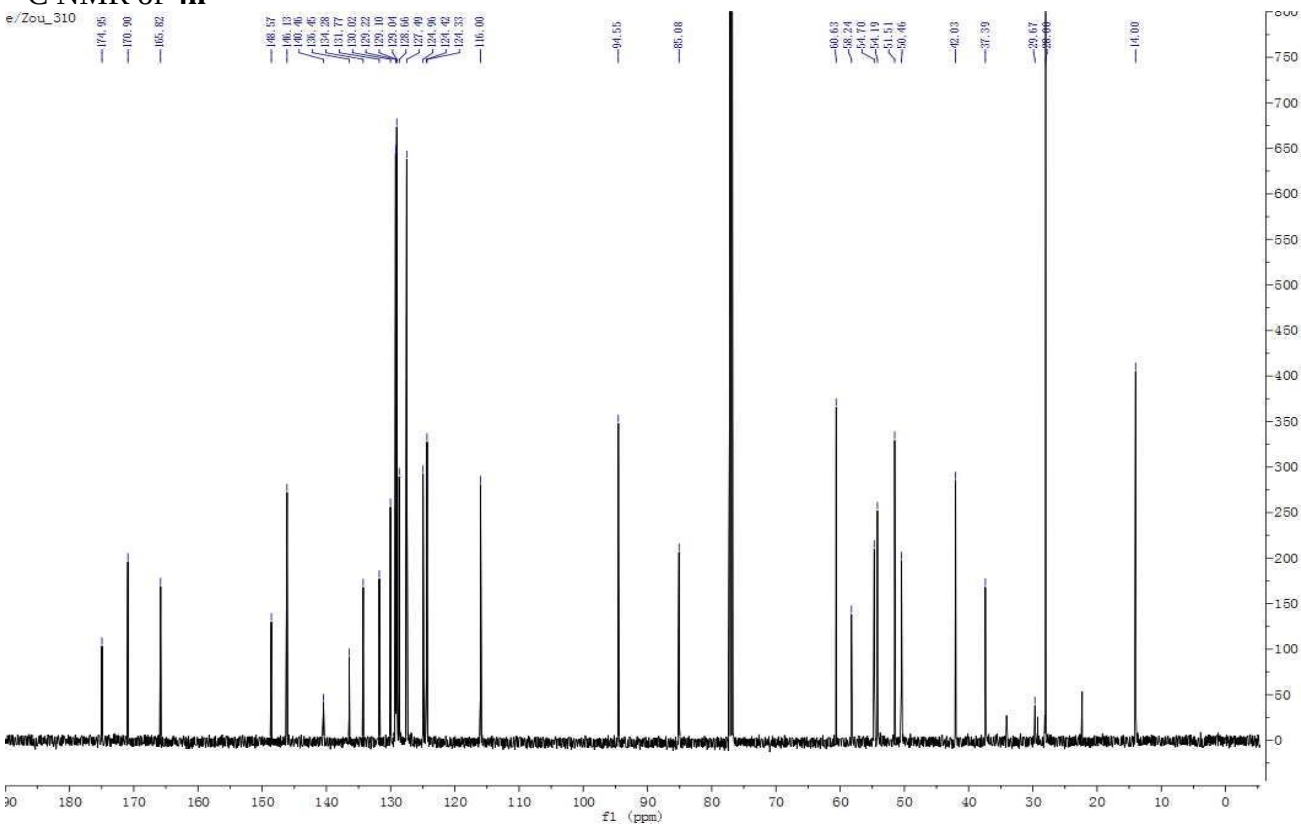
Name Zou 325 TLC

RT [min]	Type	Area%	Area	Height	Width [min]
3.94	BV	0.48	80.12	7.93	0.15
4.13	VV	0.28	46.80	6.30	0.11
4.90	VV	0.37	62.05	8.78	0.11
7.78	BB	0.83	140.20	5.71	0.35
9.36	BV	0.40	67.90	3.02	0.33
9.83	VB	0.56	93.73	2.55	0.50
12.51	MF	90.40	15233.67	389.64	0.65
13.61	FM	3.28	553.13	14.27	0.65
18.16	BV	2.92	492.76	9.82	0.75
19.52	VV	0.48	80.24	2.63	0.45
	Sum	100.00	16850.60		

^{1}H NMR of **4h**



^{13}C NMR of **4h**



Chiral HPLC analysis: rac-**4h**

AK Prof. Enders - Analytiklabor 4.04

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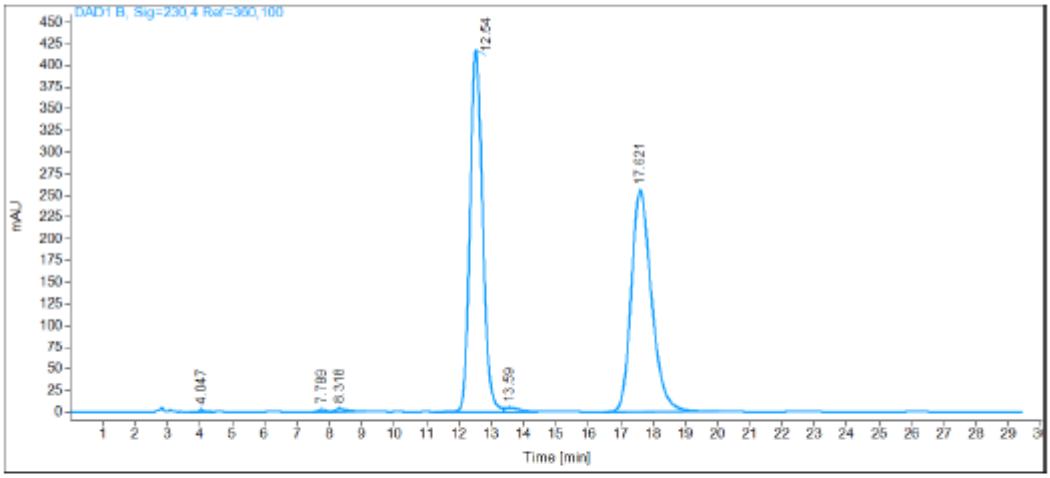
Sample name: Zou 263 rac

Data file: C:\SNOOPY\ZOU\ZOU 263 RAC IC.D
Description: Laufmittel: n-Heptan/EtOH 97:3 Die Probe ist DCM/LM gelöst.

Injection date: 6/26/2014 8:42:20 AM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 27 bar **Start flow:** 0.700 ml/min **Column oven:** 29.98 °C



Name Zou 263 rac

RT [min]	Type	Area%	Area	Height	Width [min]
4.05	BV	0.15	33.86	3.02	0.15
7.79	BV	0.20	46.68	3.02	0.24
8.32	VB	0.46	105.17	3.57	0.41
12.54	BV	49.46	11281.25	417.56	0.42
13.59	VV	0.74	169.44	4.73	0.53
17.62	BB	48.98	11170.14	255.35	0.67
	Sum	100.00	22806.54		

Chiral HPLC analysis: **4h**

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Sample name: Zou 310

Data file: C:\SNOOPY\ZOU\310IC.D

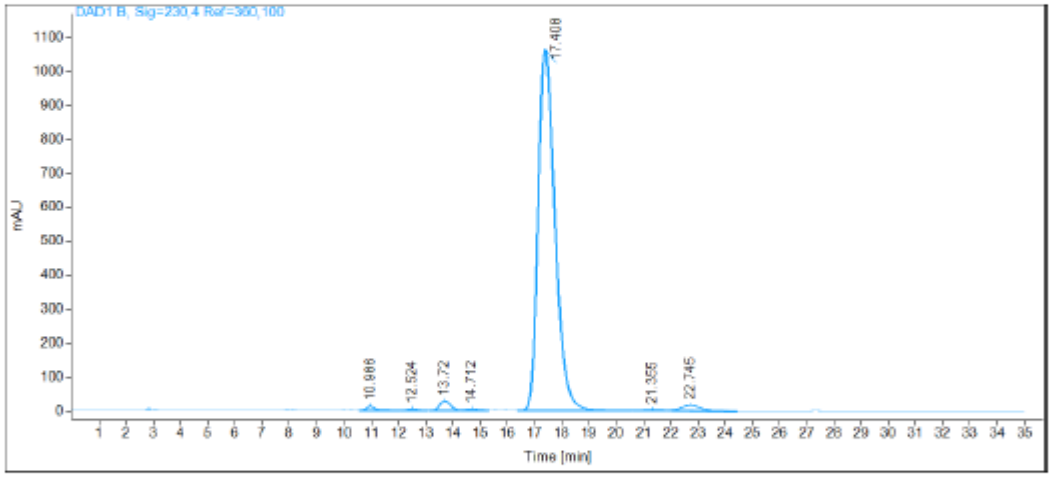
Description: Laufmittel: n-Heptan/EtOH 97:3;
Probe ist in LM/DCM gelöst.

Injection date: 8/25/2014 4:36:20 PM

Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

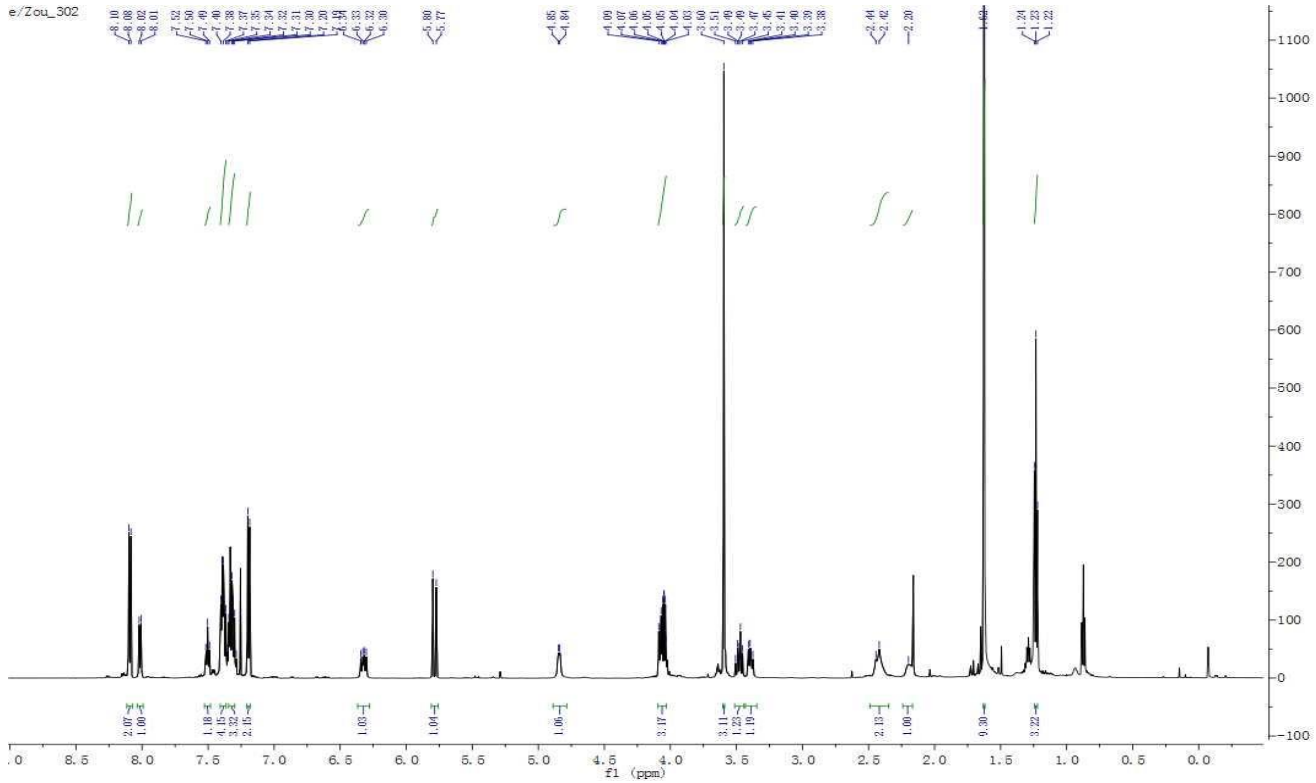
Pressure at start: 29 bar **Start flow:** 0.700 ml/min **Column oven:** 29.98 °C



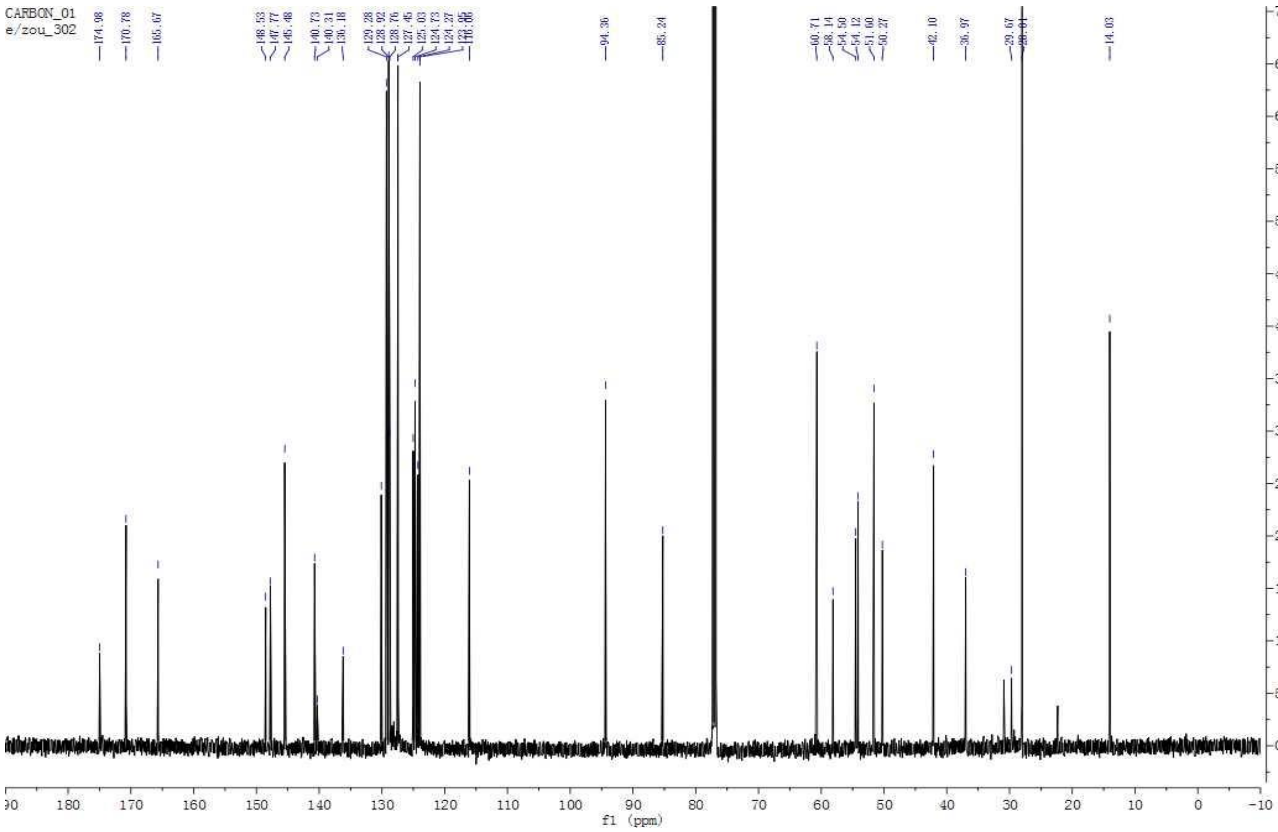
Name Zou 310

RT [min]	Type	Area%	Area	Height	Width [min]
10.99	VB	0.77	370.70	12.58	0.43
12.52	BB	0.34	165.56	6.42	0.40
13.72	BV	1.69	818.99	27.95	0.45
14.71	VV	0.46	222.62	6.31	0.53
17.41	BB	94.65	45762.80	1063.97	0.66
21.36	BV	0.32	153.49	3.39	0.71
22.74	VB	1.77	854.53	16.06	0.82
	Sum	100.00	48348.69		

^{1}H NMR of **4i**



^{13}C NMR of **4i**



Chiral HPLC analysis: rac-**4i**

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Sample name: Zou 345 rac

Data file: C:\SNOOPY\ZOU\ZOU 345 RAC NIA.D

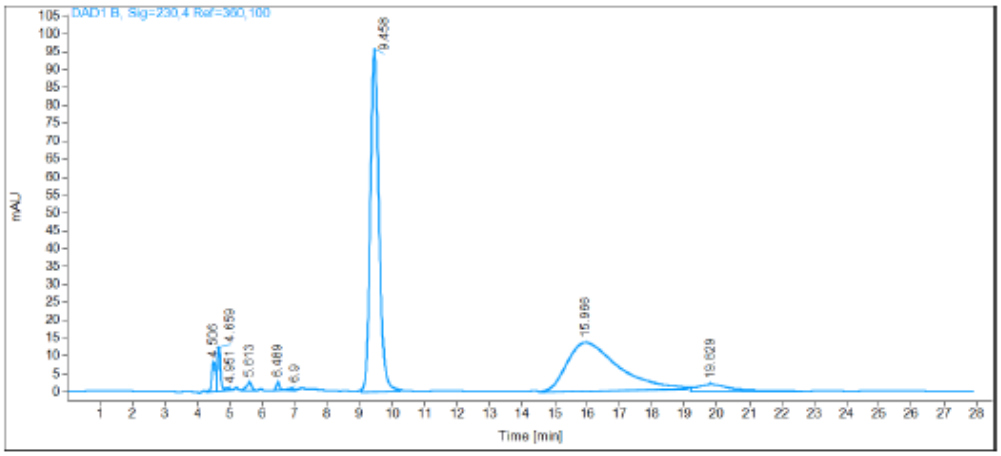
Description: Laufmittel: n-Heptan/EtOH 7:3 Die Probe ist DCM/LM gelöst.

Injection date: 9/2/2014 2:05:42 PM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 42 bar **Start flow:** 0.700 ml/min **Column oven:** 29.98 °C



Name Zou 345 rac

RT [min]	Type	Area%	Area	Height	Width [min]
4.51	VV	1.83	66.16	8.35	0.12
4.66	VV	2.16	78.10	12.48	0.09
4.95	VB	0.19	6.85	0.68	0.14
5.61	VV	0.65	23.62	2.15	0.16
6.49	BB	0.43	15.50	2.25	0.11
6.90	BV	0.20	7.14	0.49	0.20
9.46	MM	48.88	1766.74	95.85	0.31
15.97	MM	41.28	1491.92	13.53	1.84
19.83	VB	4.38	158.24	1.98	1.08
	Sum	100.00	3614.26		

Chiral HPLC analysis: **4i**

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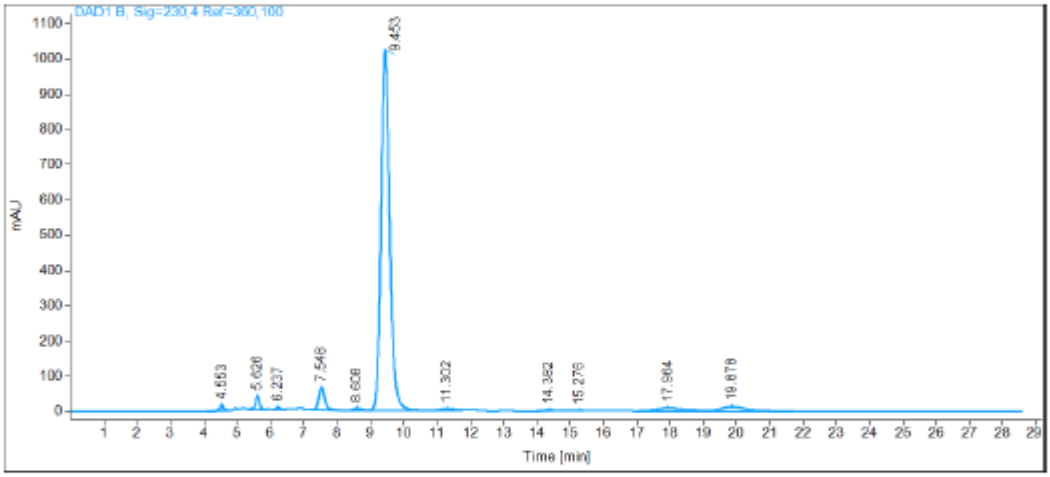
Sample name: Zou 302

Data file: C:\SNOOPY\ZOU\ZOU 302 IA.D
Description: Laufmittel: n-Heptan/EtOH 7:3 Die Probe ist DCM/LM gelöst.

Injection date: 9/2/2014 1:35:13 PM
Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

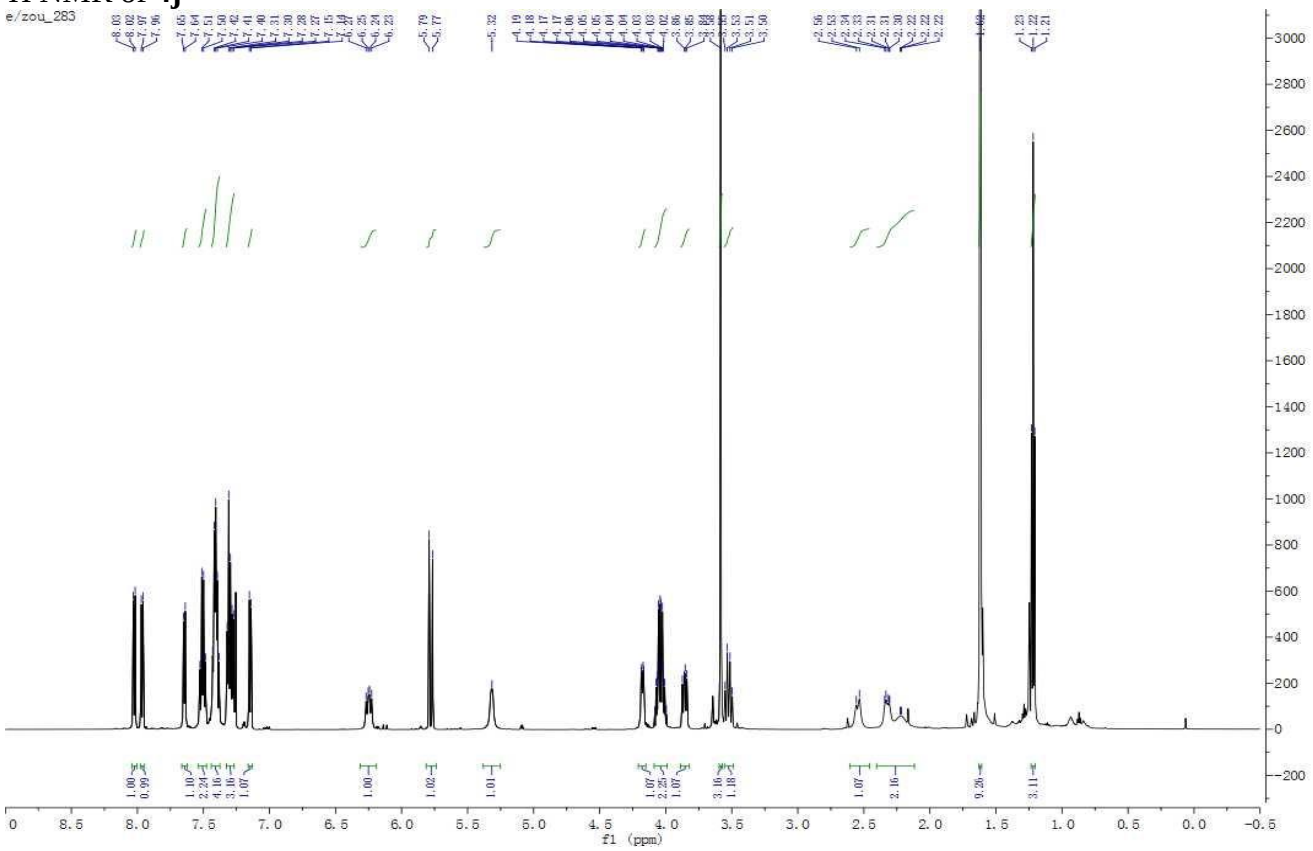
Pressure at start: 42 bar **Start flow:** 0.700 ml/min **Column oven:** 29.99 °C



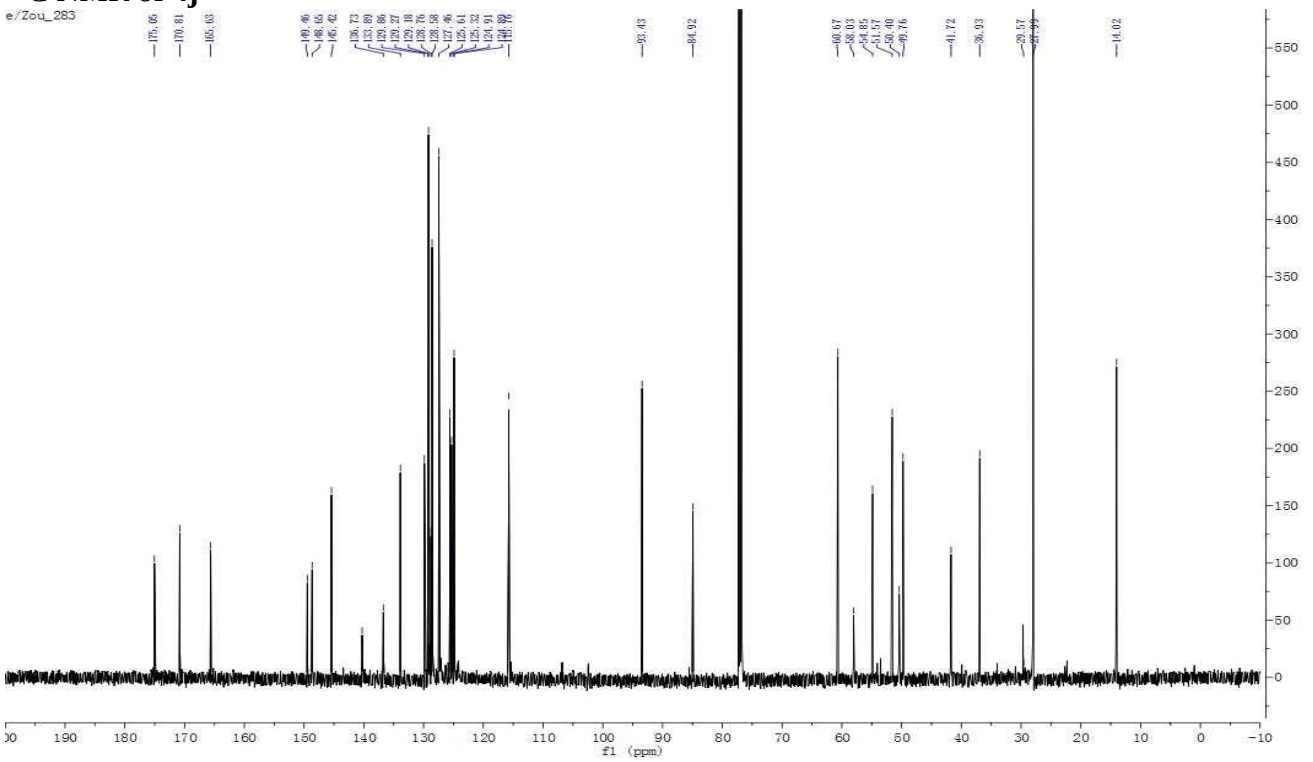
Name Zou 302

RT [min]	Type	Area%	Area	Height	Width [min]
4.55	BB	0.66	143.43	17.66	0.12
5.63	VV	1.55	337.05	37.96	0.13
6.24	BB	0.31	66.37	7.85	0.13
7.55	BB	3.78	820.58	65.35	0.19
8.61	BV	0.49	106.52	6.11	0.26
9.45	VV	86.81	18841.98	1023.63	0.28
11.30	VV	0.98	211.93	5.65	0.59
14.38	MM	0.17	37.12	2.44	0.25
15.28	MM	0.04	9.55	0.27	0.45
17.96	BV	2.29	497.00	8.62	0.88
19.88	VB	2.92	632.95	12.48	0.78
	Sum	100.00	21704.48		

^{1}H NMR of **4j**



^{13}C NMR of **4j**



Chiral HPLC analysis: rac-**4j**

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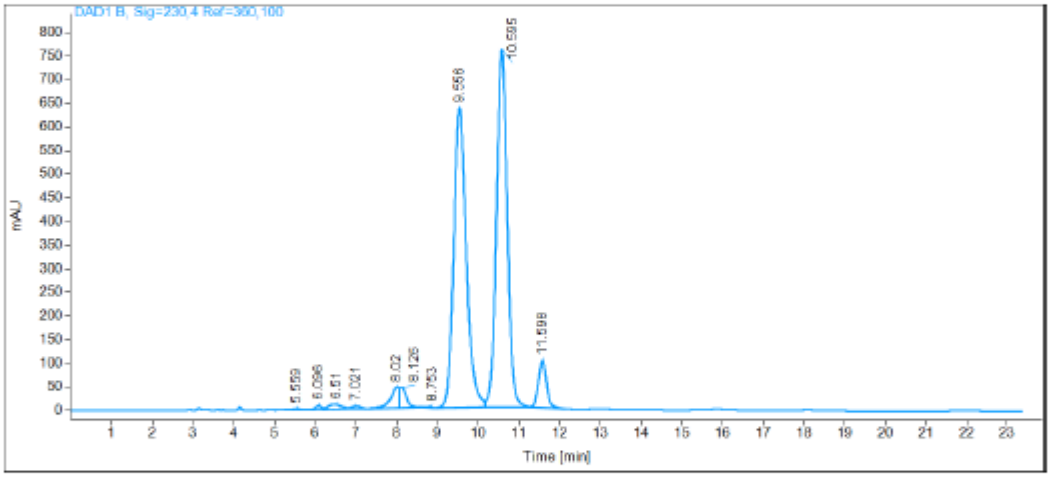
Sample name: Zou 259 rac

Data file: C:\SNOOPY\ZOU\ZOU 259 RAC 3IA.D
Description: Laufmittel: n-Heptan/EtOH 9:1 Die Probe ist DCM/LM gelöst.

Injection date: 6/23/2014 3:28:50 PM
Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 47 bar **Start flow:** 1.000 ml/min **Column oven:** 29.98 °C



Name Zou 259 rac

RT [min]	Type	Area%	Area	Height	Width [min]
5.56	VB	0.13	39.77	2.81	0.20
6.10	BV	0.26	78.15	7.88	0.15
6.51	VV	0.75	228.39	10.48	0.29
7.02	VB	0.30	91.68	6.19	0.22
8.02	BV	1.98	602.73	43.35	0.20
8.13	VB	1.69	513.65	43.30	0.18
8.75	BB	0.04	11.32	1.20	0.15
9.56	BV	45.07	13731.75	633.11	0.33
10.59	VB	45.25	13787.54	756.58	0.28
11.60	BB	4.55	1384.87	99.54	0.21
	Sum	100.00	30469.85		

Chiral HPLC analysis: **4j**

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Sample name: Zou 283

Data file: C:\SNOOPY\ZOU\ZOU 283 IA.D

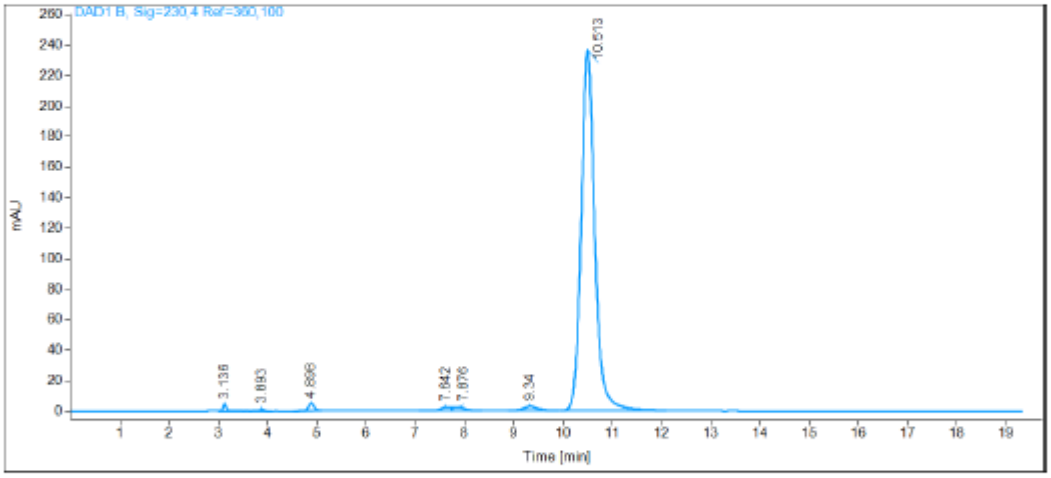
Description: Laufmittel: n-Heptan/EtOH 9:1 Die Probe ist DCM/LM gelöst.

Injection date: 7/1/2014 2:36:11 PM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

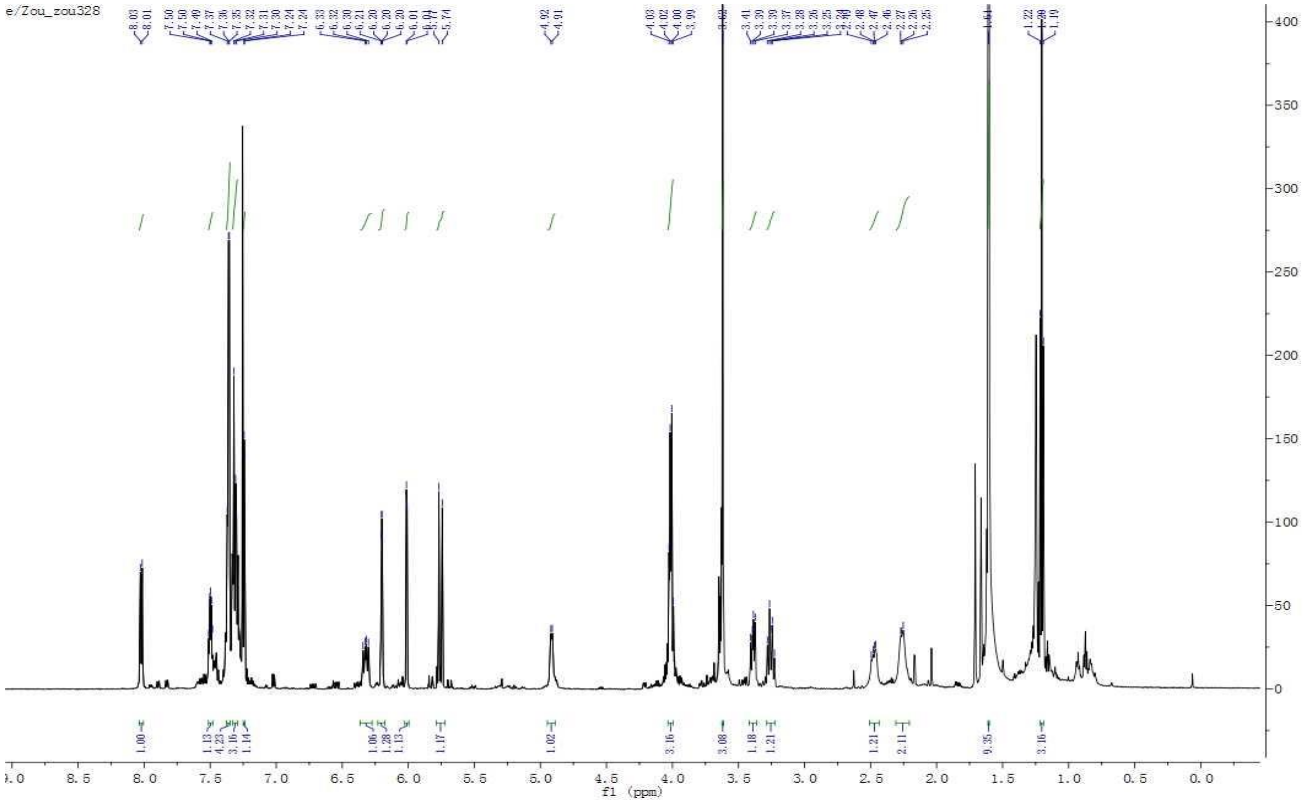
Pressure at start: 46 bar **Start flow:** 1.000 ml/min **Column oven:** 29.98 °C



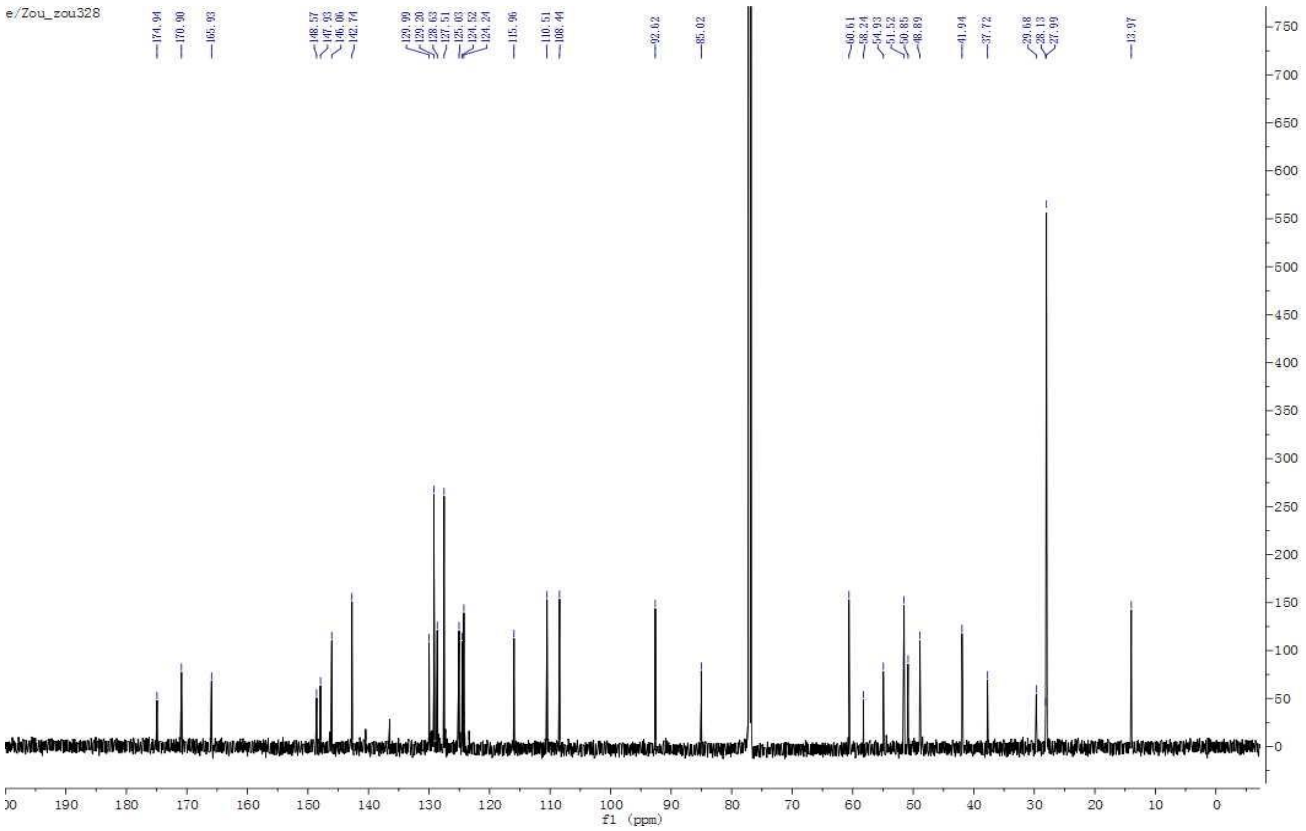
Name Zou 283

RT [min]	Type	Area%	Area	Height	Width [min]
3.14	VV	0.51	24.42	4.15	0.09
3.89	VV	0.17	7.96	1.24	0.09
4.90	BB	0.86	40.92	4.81	0.13
7.64	BV	0.78	37.06	2.57	0.21
7.88	VV	0.89	42.28	2.52	0.25
9.34	BB	1.28	61.09	2.77	0.34
10.51	BB	95.52	4555.23	236.59	0.29
	Sum	100.00	4768.97		

^{1}H NMR of **4k**



^{13}C NMR of **4k**



Chiral HPLC analysis: rac-**4k** (note: An eluent n-Heptane/isopropanol = 9:1)

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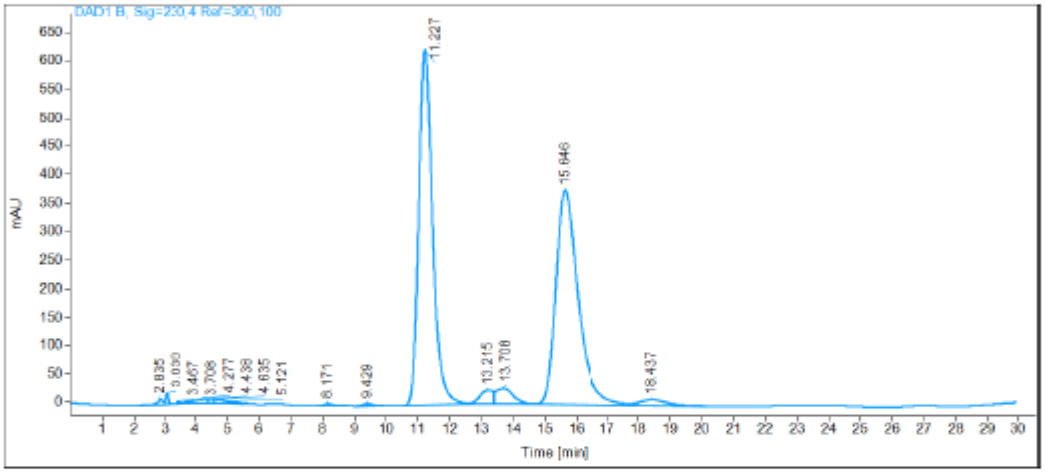
Sample name: Zou 309 rac
Data file: C:\SNOOPY\ZOU\309RNIC.D
Description: Laufmittel: n-Heptan/EtOH 97:3; Probe ist in LM/DCM gelöst.
Injection date: 8/15/2014 9:18:36 AM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 29 bar **Start flow:** 0.700 ml/min **Column oven:** 30.01 °C



Name Zou 309 rac

RT [min]	Type	Area%	Area	Height	Width [min]
2.84	BV	0.26	107.11	10.14	0.15
3.04	VB	0.26	106.82	20.30	0.08
3.47	BB	0.05	21.65	4.22	0.08
3.71	BV	0.05	20.40	3.05	0.10
4.28	VV	0.53	215.09	9.89	0.28
4.44	VV	0.21	84.20	8.03	0.14
4.64	VV	0.41	164.40	7.14	0.35
5.12	VB	0.17	68.65	4.15	0.26
8.17	VB	0.20	79.19	3.39	0.33
9.43	BV	0.21	86.29	3.80	0.36
11.23	BB	46.25	18772.53	624.27	0.46
13.22	BV	1.65	668.92	23.73	0.44
13.71	VB	2.58	1048.67	27.58	0.56
15.65	BV	45.68	18539.09	375.47	0.75
18.44	VB	1.49	604.22	10.04	0.90
	Sum	100.00	40587.22		

Chiral HPLC analysis: **4k** (note: An eluent n-Heptane/isopropanol = 9:1 was used)

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Sample name: Zou 328

Data file: C:\SNOOPY\ZOU\328IC.D

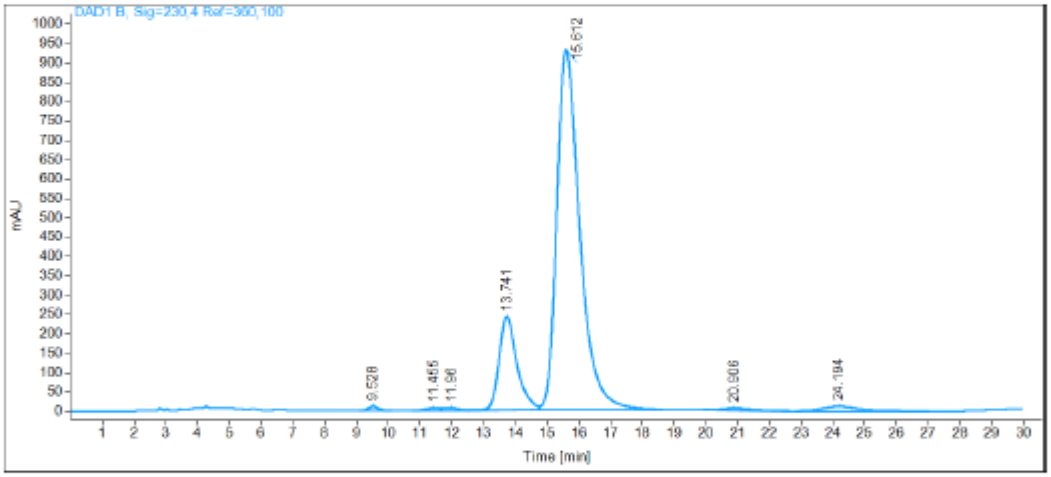
Description: Laufmittel: n-Heptan/EtOH 97:3;
Probe ist in LM/DCM gelöst.

Injection date: 8/15/2014 8:47:30 AM

Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

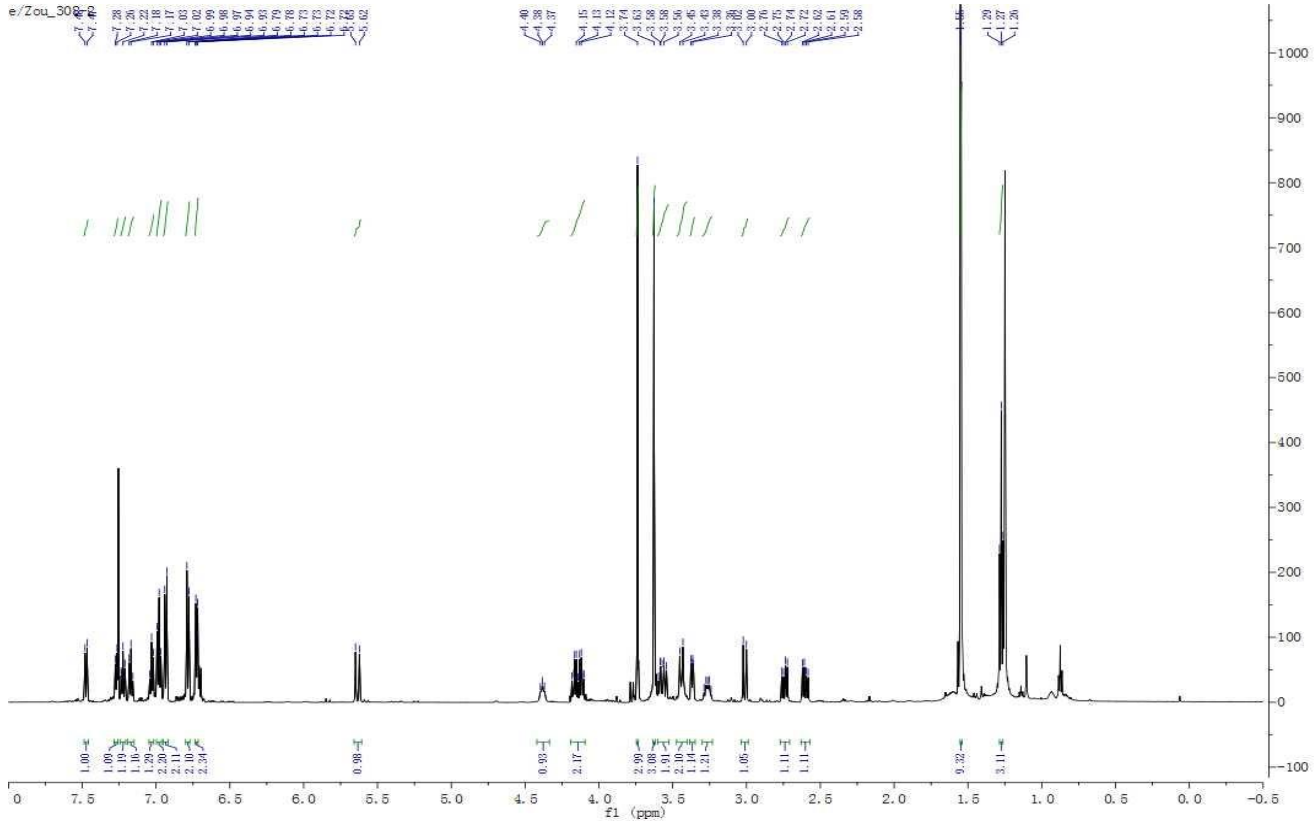
Pressure at start: 29 bar **Start flow:** 0.700 ml/min **Column oven:** 30 °C



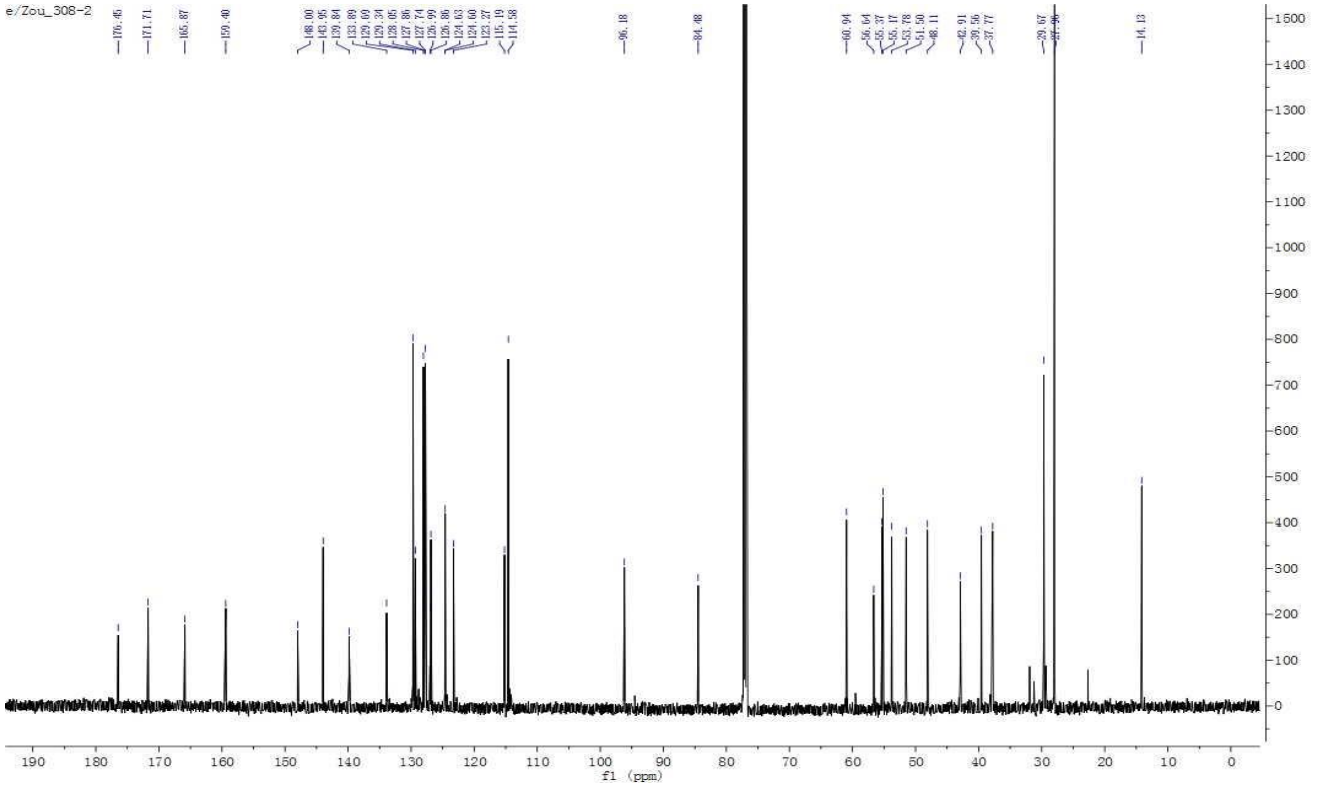
Name Zou 328

RT [min]	Type	Area%	Area	Height	Width [min]
9.53	BB	0.43	253.58	11.48	0.34
11.46	BV	0.33	194.36	6.07	0.50
11.96	VB	0.35	202.57	6.69	0.46
13.74	BV	16.34	9552.84	241.64	0.60
15.61	VB	80.16	46863.13	930.84	0.76
20.91	BB	0.65	381.84	6.01	0.94
24.19	BB	1.73	1011.19	12.18	1.21
	Sum	100.00	58459.50		

^{1}H NMR of **4l**



^{13}C NMR of **4l**



Chiral HPLC analysis: rac-**4l**

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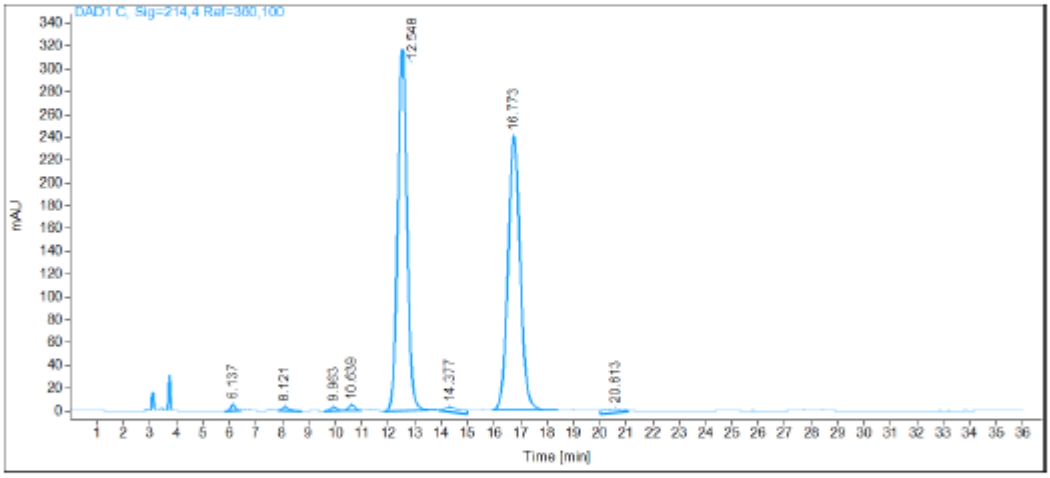
Sample name: Zou 342

Data file: C:\SNOOPY\ZOU\ZOU 342 IA.D
Description: Laufmittel: n-Heptan/IP 9:1 Die Probe ist DCM/LM gelöst.

Injection date: 8/29/2014 8:29:29 AM
Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 50 bar **Start flow:** 1.000 ml/min **Column oven:** 30 °C



Name Zou 342

RT [min]	Type	Area%	Area	Height	Width [min]
6.14	BB	0.41	66.87	5.39	0.19
8.12	BB	0.39	63.05	3.12	0.30
9.96	BB	0.37	59.31	3.28	0.29
10.64	BB	0.49	78.90	4.34	0.29
12.55	BB	48.35	7817.13	316.67	0.38
14.38	MM	1.06	172.15	3.87	0.74
16.77	BB	47.83	7732.28	239.76	0.50
20.61	MM	1.09	176.95	3.39	0.65
	Sum	100.00	16166.64		

Chiral HPLC analysis: **4l** (note: An eluent n-Heptane/isopropanol = 9:1 was used)

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Sample name: Zou 354

Data file: C:\SNOOPY\ZOU\354IA.D

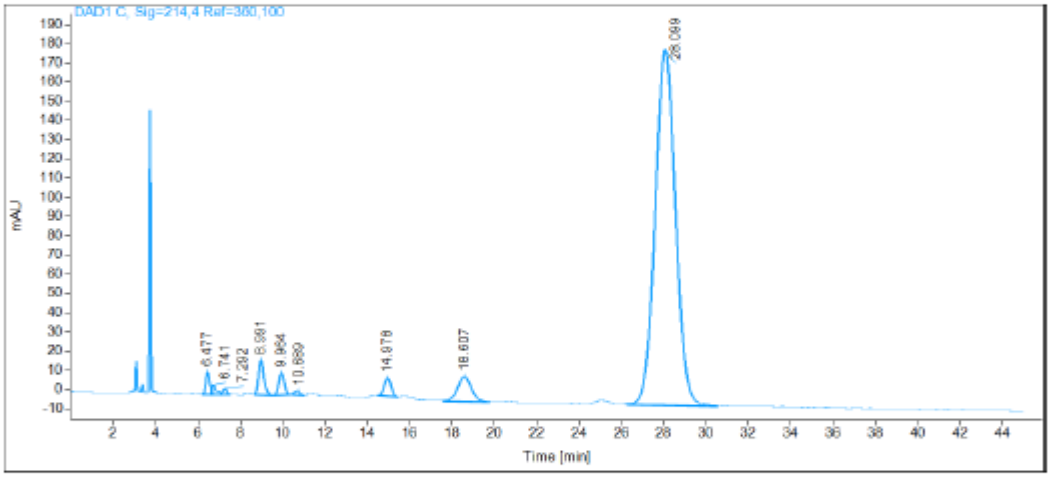
Description: Laufmittel: n-Heptan/IP 95:5;
Probe ist in LM/DCM gelöst.

Injection date: 9/4/2014 11:49:04 AM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

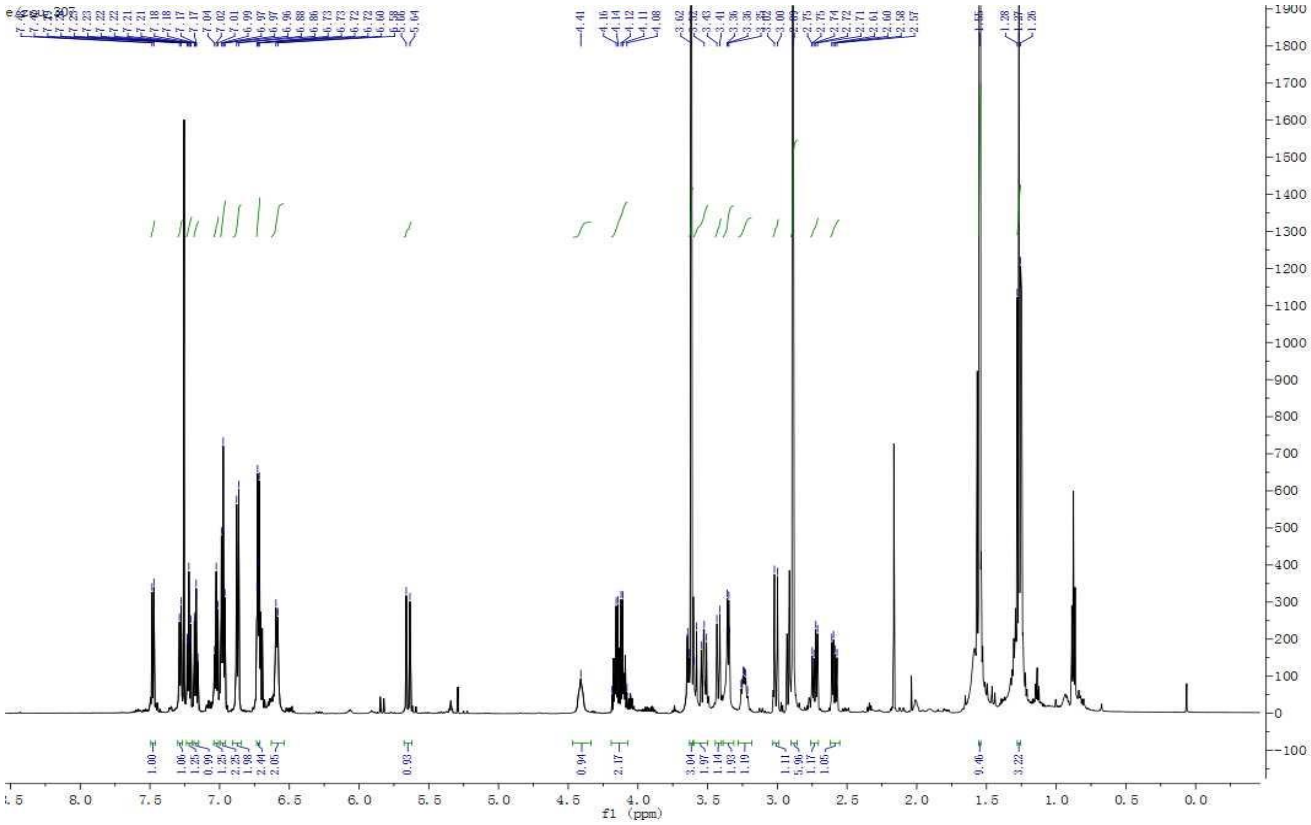
Pressure at start: 50 bar **Start flow:** 1.000 ml/min **Column oven:** 29.99 °C



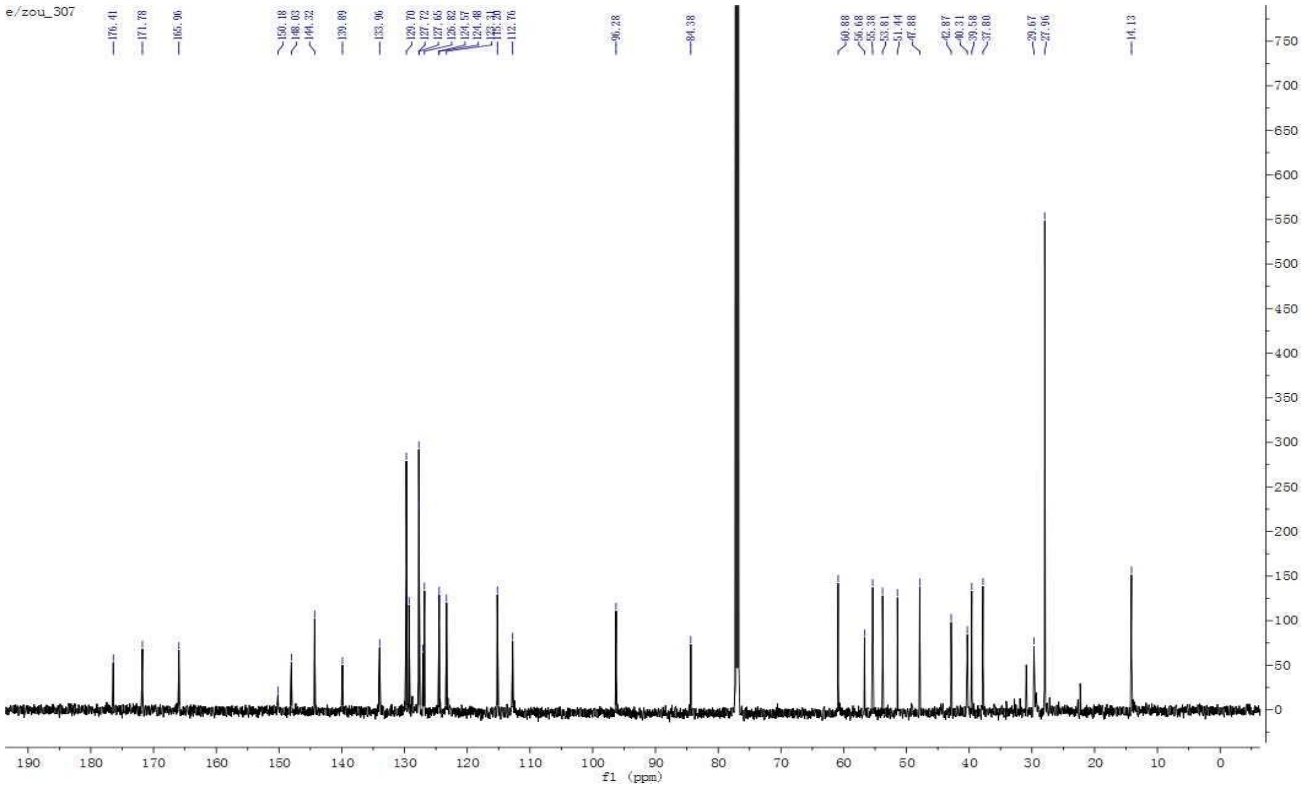
Name Zou 354

RT [min]	Type	Area%	Area	Height	Width [min]
6.48	BV	1.06	148.41	11.40	0.20
6.74	VV	0.53	73.70	4.89	0.21
7.29	VB	0.26	36.67	2.91	0.19
8.99	BB	2.28	319.16	17.92	0.27
9.96	BB	1.50	210.38	11.36	0.29
10.69	BB	0.27	37.24	2.22	0.27
14.98	BB	1.60	223.62	9.64	0.37
18.61	BB	4.24	593.15	12.87	0.74
28.10	BB	88.26	12351.44	185.05	1.04
	Sum	100.00	13993.76		

^{1}H NMR of **4m**



^{13}C NMR of **4m**



Chiral HPLC analysis: rac-**4m**

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Sample name: Zou 343

Data file: C:\SNOOPY\ZOU\343IA.D

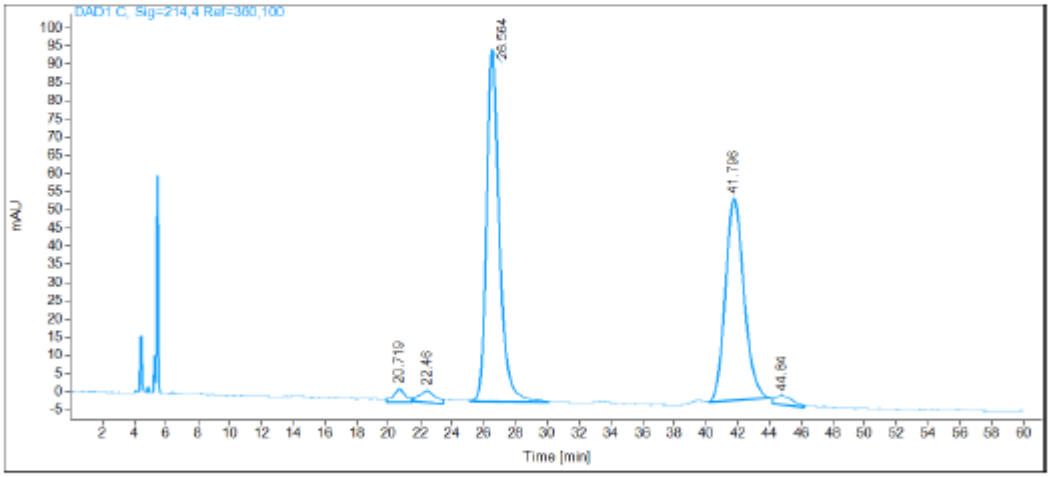
Description: Laufmittel: n-Heptan/IP 95:5;
Probe ist in LM/DCM gelöst.

Injection date: 8/28/2014 4:26:56 PM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 33 bar **Start flow:** 0.700 ml/min **Column oven:** 30 °C



Name Zou 343

RT [min]	Type	Area%	Area	Height	Width [min]
20.72	MM	1.78	185.17	3.60	0.86
22.46	MM	2.01	209.32	3.14	1.11
26.56	BB	51.26	5344.58	96.64	0.83
41.80	BB	43.20	4504.24	55.45	1.23
44.84	MM	1.75	182.90	2.30	1.32
	Sum	100.00	10426.21		

Chiral HPLC analysis: **4m**

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Sample name: Zou 307

Data file: C:\SNOOPY\ZOU\307IA.D

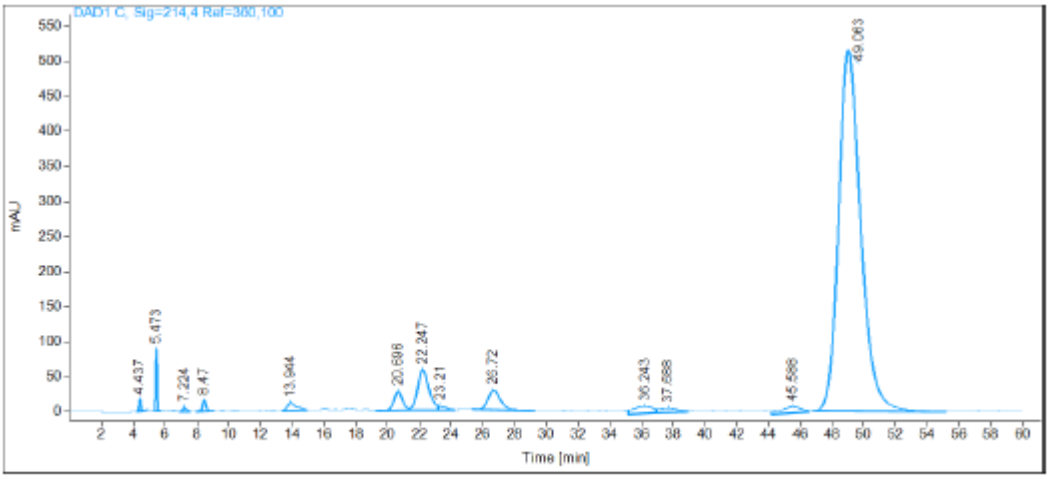
Description: Laufmittel: n-Heptan/IP 95:5; Probe ist in LM/DCM gelöst.

Injection date: 8/21/2014 3:30:09 PM

Acq. Analysis method: CHIRALPAKIARNP.M

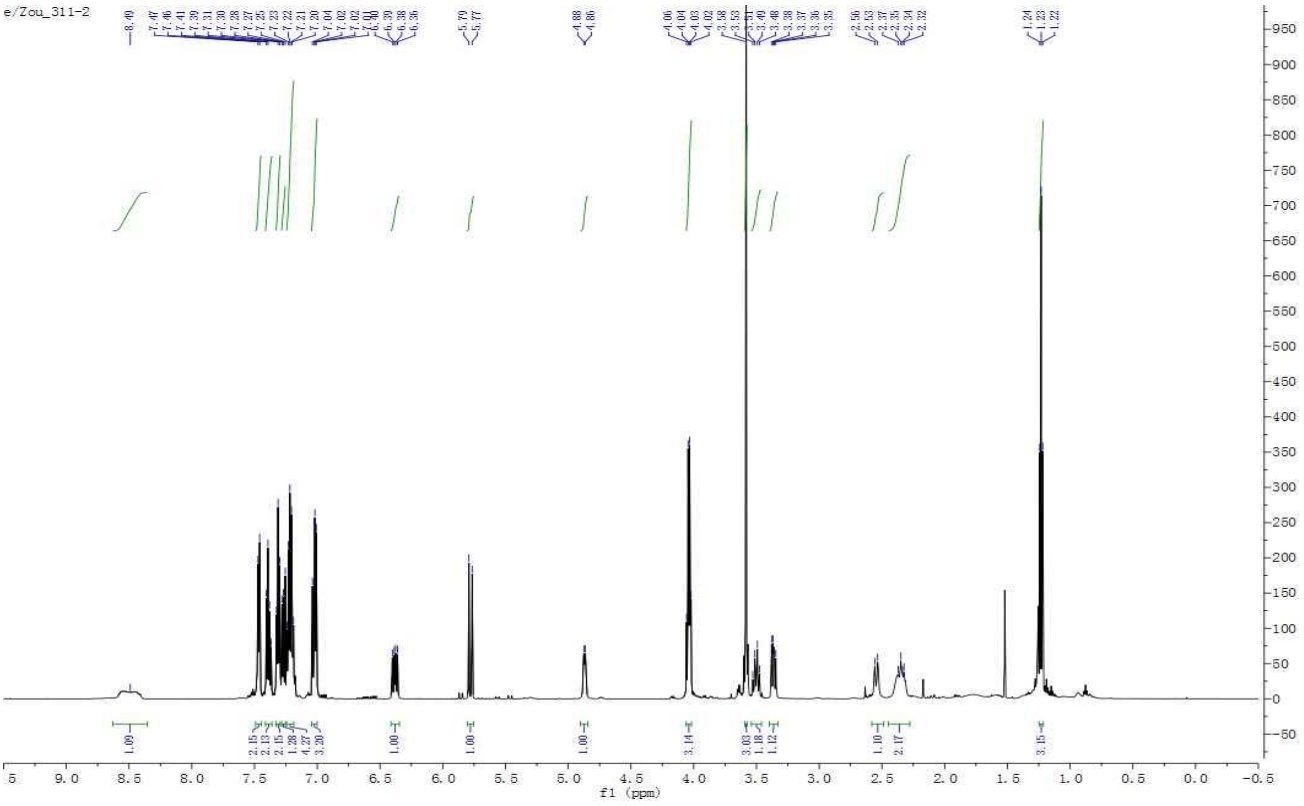
Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 32 bar **Start flow:** 0.700 ml/min **Column oven:** 29.97 °C

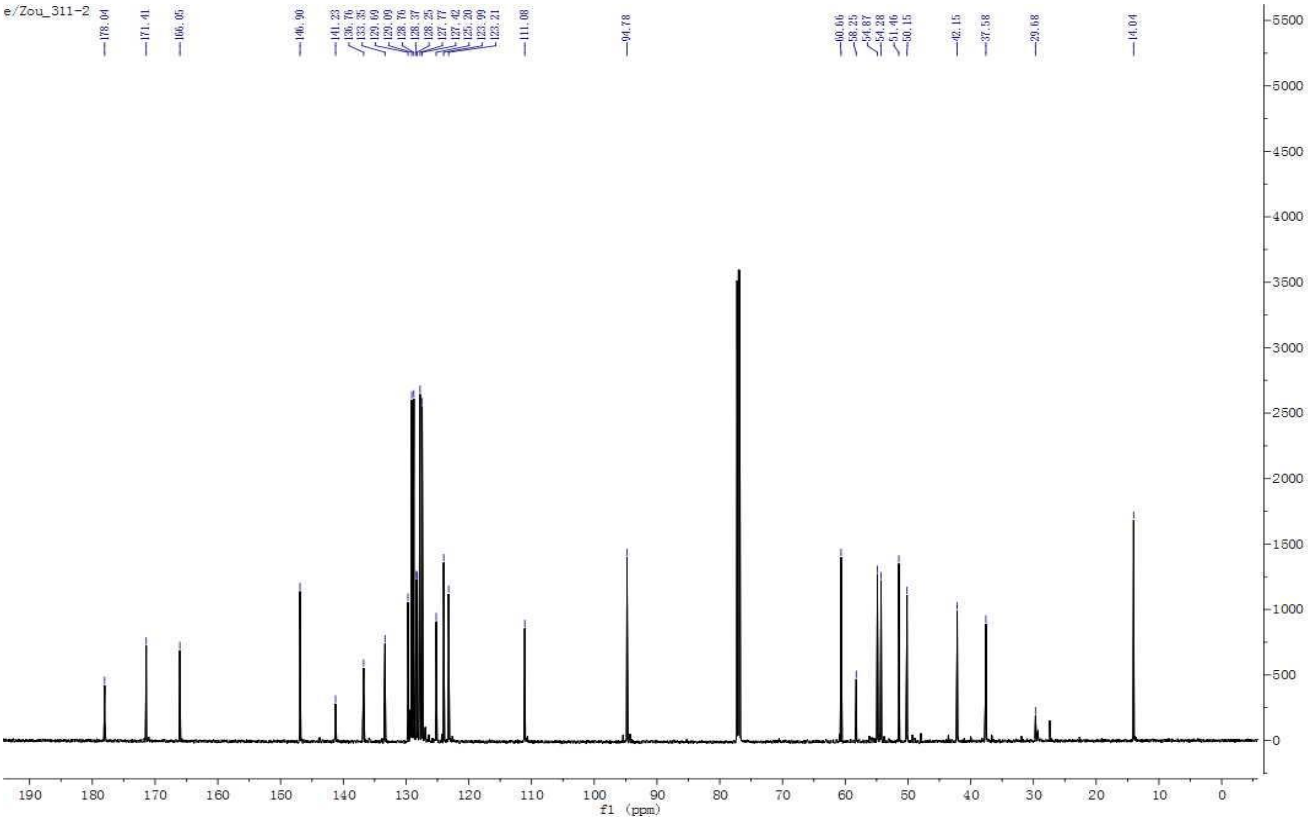


Name	Zou 307				
RT [min]	Type	Area%	Area	Height	Width [min]
4.44	BB	0.19	113.93	16.14	0.11
5.47	BB	0.94	556.60	87.75	0.10
7.22	BB	0.15	85.90	5.71	0.21
8.47	BB	0.45	263.24	15.88	0.25
13.94	BB	0.74	437.93	11.11	0.58
20.70	BV	1.75	1028.86	27.21	0.57
22.25	MF	4.76	2807.74	56.74	0.82
23.21	FM	0.29	170.09	5.52	0.51
26.72	BB	2.58	1519.25	28.02	0.82
36.24	MF	1.47	865.78	10.19	1.42
37.89	FM	0.86	508.48	6.40	1.32
45.59	MM	1.25	736.10	8.35	1.47
49.06	BB	84.57	49841.05	514.68	1.48
	Sum	100.00	58934.96		

^{1}H NMR of **6**



^{13}C NMR of **6**



Chiral HPLC analysis: rac-**6**

AK Prof. Enders - Analytiklabor 4.04

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Sample name: Zou 293 rac

Data file: C:\SNOOPY\ZOU\293R2IC.D

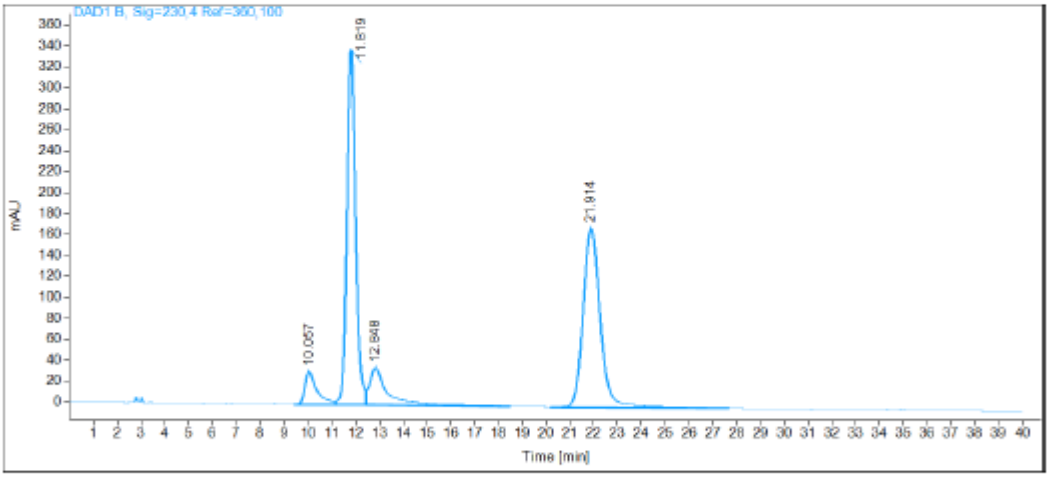
Description: Laufmittel: n-Heptan/EtOH 9:1; Probe ist in LM/DCM gelöst

Injection date: 9/24/2014 3:54:22 PM

Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 24 bar **Start flow:** 0.700 ml/min **Column oven:** 30 °C



Name Zou 293 rac

RT [min]	Type	Area%	Area	Height	Width [min]
10.06	BV	5.53	1120.57	31.44	0.51
11.82	VV	42.80	8670.87	339.38	0.39
12.85	VB	9.44	1912.01	35.35	0.74
21.91	BB	42.23	8554.98	170.39	0.77
	Sum	100.00	20258.43		

Chiral HPLC analysis: **6**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

Sample name: Zou 373

Data file: C:\SNOOPY\ZOU\373IC.D

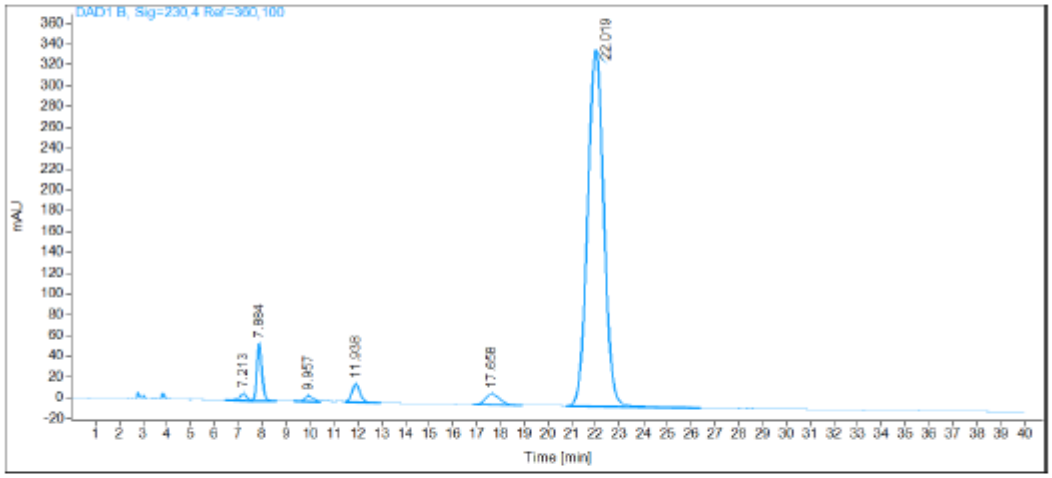
Description: Laufmittel: n-Heptan/EtOH 9:1; Probe ist in LM/DCM gelöst

Injection date: 9/24/2014 3:13:14 PM

Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 24 bar **Start flow:** 0.700 ml/min **Column oven:** 30 °C



Name	Zou 373				
RT [min]	Type	Area%	Area	Height	Width [min]
7.21	BV	0.77	138.52	6.55	0.32
7.88	VB	4.64	840.29	54.47	0.24
9.96	BV	0.74	134.53	5.27	0.39
11.94	VB	2.40	434.64	17.51	0.38
17.66	BB	2.31	417.37	10.11	0.64
22.02	BB	89.14	16127.83	342.30	0.74
	Sum	100.00	18093.17		