Electronic Supplementary Material (ESI) for ChemComm.

Content

1. General Methods

The products were purified by column chromatography on Merck silica gel 60, particle size 0.040-0.063 mm (230-240 mesh, flash). For thin-layer chromatography (TLC) analysis, SIL G-25 UV254 from MACHEREY&NAGEL were used. Visualization of the developed TLC plates was performed with ultraviolet irradiation (254 nm). ^{1}H- and ^{13}C-NMR spectra were recorded at ambient temperature on Inova 400 or VNMRS 600 instruments with tetramethylsilane as an internal standard. Mass spectra and high resolution mass spectra were acquired on a Finnigan MAT 95 (EI/CI) or on a ThermoFisher Scientific LTQ Orbitrap XL (ESI). IR spectra were taken on a PerkinElmer Spectrum 100 FT-IR Spectrometer. Optical rotation values were measured on a Perkin-Elmer 241 polarimeter. Analytical HPLC was performed on a Hewlett-Packard 1100 Series instrument using chiral stationary phases (Chiralpak IA, IB, IC, AD, AS).

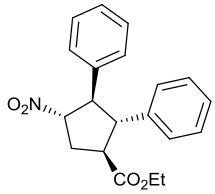
2. Materials

All reactions were carried out under argon. Dry dichloromethane was purchased from Acros. All other chemicals were used without further purification. Triazolium salts **A-F** were prepared according to known literature procedures.[1] (*E*)-2-nitroallylic acetates were synthesized according to literature.[2]

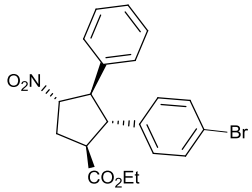
3. General procedure

Enals (0.75 mmol), (*E*)-2-nitroallylic acetates (0.5 mmol), NHC pre-catalyst (10 mol%) and K_3PO_4 (0.5 mmol) in 2 mL $CHCl_3$:EtOH (10:1) were stirred for 60 h at −10 °C under Argon. Flash Chromatography (pentane:ether = 30:1) afforded the desired products.

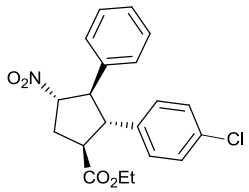
4. Characterization Data



The compound **3a** was prepared according to the general procedure. The product was obtained as a colorless solid (89 mg, 52% yield); Melting point: 97-99 °C; Enantiomeric ratio was determined as 93:7 by HPLC [Chiralpak IA, elute: *n*-Heptane/EtOH = 97:3, detector: 214 nm, flow rate: 0.7 mL/min), 30 °C, t_1 = 12.30 min (minor), t_2 = 14.08 min (major)]; $[\alpha]_D^{20}$= + 6.4 (c = 0.5, $CHCl_3$);
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 6H), 7.16 – 7.14 (m, 2H), 7.12 – 7.10 (m, 2H), 5.18 – 5.14 (m, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.88 (dd, *J* = 12.0 Hz, 7.8 Hz, 1H), 3.55 – 3.51 (m, 1H), 3.46 – 3.41 (m, 1H), 2.86 – 2.80 (m, 1H), 2.77 – 2.72 (m, 1H), 1.11 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.3, 138.6, 137.9, 128.9 (2C), 128.6 (2C), 127.8 (2C), 127.5 (2C), 127.4 (2C), 91.1, 61.0, 58.9, 56.3, 49.9, 35.0, 14.0.
IR (ATR): 3063, 3031, 2980, 2933, 1722, 1603, 1538, 1496, 1453, 1374, 1292, 1268, 1216, 1182, 1095, 1024, 967, 910, 858, 834, 804, 759, 698, 661 cm^{-1};
HRMS (ESI) m/z Calculated for $C_{20}H_{21}NO_4Na$ $[M+Na]^+$ 362.1363, found 362.1380.



The compound **3b** was prepared according to the general procedure. The product was obtained as a colorless solid (110 mg, 53% yield); Melting point: 99-101 °C; Enantiomeric ratio was determined as 86:14 by HPLC [Chiralpak IA, elute: *n*-Heptan/*i*-PrOH = 97:3, detector: 230 nm, flow rate: 0.7 mL/min), 30 °C, t_1 = 17.01 min (major), t_2 = 18.36 min (minor)]; $[\alpha]_D^{20}$ = – 13.8 (c = 0.50, $CHCl_3$);
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.35 (m, 2H), 7.28 – 7.22 (m, 3H), 7.10 – 7.08 (m, 2H), 7.03 – 7.02 (m, 2H), 5.16 – 5.12 (m, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.80 (dd, *J* =7.2 Hz, *J* =11.4Hz, 1H), 3.50 – 3.47 (m, 1H), 3.42 – 3.37 (m, 1H), 2.84 – 2.80 (m, 1H), 2.76 – 2.70 (m, 1H), 1.13 (t, *J* = 7.2 Hz, 3H);
^{13}C NMR (150 MHz, $CDCl_3$) δ 172.9, 137.6, 137.5, 131.8 (2C) , 129.2 (2C), 129.0 (2C), 127.9, 127.3 (2C), 121.3, 90.9, 61.1, 58.9, 55.7, 49.7, 34.9, 14.1;
IR (ATR): 3031, 2965, 1720, 1598, 1544, 1490, 1452, 1376, 1293, 1259, 1216, 1184, 1080, 1014, 798, 695 cm^{-1};
HRMS (EI) m/z Calculated for $C_{20}H_{20}BrNO_4$ 417.0570, found 417.0576.



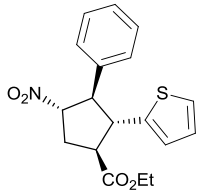
The compound **3c** was prepared according to the general procedure. The product was obtained as a colorless solid (90 mg, 48% yield); Melting point: 92-94 °C; Enantiomeric ratio was determined as 88:12 by HPLC [Chiralpak IA, elute: *n*-Heptan/*i*-PrOH = 9:1, detector: 230 nm, flow rate: 0.7 mL/min), 30 °C, t_1 = 10.09 min (major), t_2 = 10.70 min (minor)]; $[\alpha]_D^{20}$ = – 22.7 (c = 0.50, $CHCl_3$);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 5H), 7.12 – 7.07 (m, 4H), 5.16 – 5.12 (m, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.81 (dd, *J* = 12.0, 7.8 Hz, 1H), 3.53 – 3.48 (m, 1H), 3.42 – 3.37 (m, 1H), 2.84 – 2.80 (m, 1H), 2.76 – 2.71 (m, 1H), 1.13 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0 , 137.6 , 137.0 , 133.2 , 129.0 (2C) , 128.9 (2C) , 128.8 (2C) , 127.9, 127.3 (2C), 90.9 , 61.1 , 59.0 , 55.7 , 49.8 , 35.0 , 14.1 .

IR (ATR): 3060, 3031, 2980, 1720, 1599, 1544, 1492, 1451, 1374, 1290, 1257, 1183, 1091, 1016, 966, 912, 820, 756, 697 cm^{-1};

HRMS (EI) m/z Calculated for $C_{20}H_{20}ClNO_4$ 373.1075, found 373.1076.



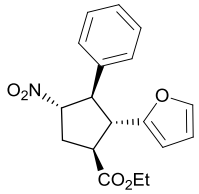
The compound **3d** was prepared according to the general procedure. The product was obtained as a colorless solid (80 mg, 46% yield); Melting point: 77-79 °C; Enantiomeric ratio was determined as 91.5:8.5 by HPLC [Chiralpak IC, elute: *n*-Heptan/*i*-PrOH = 97:3, detector: 230 nm, flow rate: 0.7 mL/min), 30 °C, t_1 = 9.20 min (minor), t_2 = 10.96 min (major)]; $[\alpha]_D^{20}$ = + 12.8(c = 0.50, $CHCl_3$);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.27 – 7.24 (m, 1H), 7.21 – 7.18 (m, 2H), 7.12 (dd, *J* = 5.4, 1.2 Hz, 1H), 6.84 (dd, *J* = 5.4, 3.6 Hz, 1H), 6.77 – 6.75 (m, 1H), 5.13 – 5.10 (m, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.93 – 3.79 (m, 2H), 3.44 – 3.39 (m, 1H), 2.85 – 2.80 (m, 1H), 2.74 – 2.68 (m, 1H), 1.20 (t, *J* = 7.2 Hz, 3H);

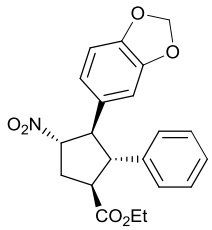
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.1, 141.9, 137.6, 128.9 (2C), 128.0, 127.5 (2C), 126.7, 125.1, 124.2, 90.9, 61.3, 59.5, 50.9, 50.7, 34.7, 14.1;

IR (ATR): 3066, 2958, 1719, 1603, 1544, 1498, 1449, 1372, 1296, 1265, 1192, 1095, 1023, 911, 852, 757, 698 cm^{-1};

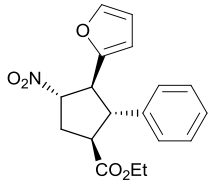
HRMS (EI) m/z Calculated for $C_{18}H_{19}NO_4S$ 345.1029, found 345.1031.



The compound **3e** was prepared according to the general procedure. The product was obtained as a colorless solid (91 mg, 55% yield); Melting point: 70-72 °C; Enantiomeric excess was determined as 92:8 by HPLC [Chiralpak AS, elute: *n*-Heptan/*i*-PrOH = 97:3, detector: 214 nm, flow rate: 0.7 mL/min), 30°C, t_1 = 13.87 min (major), t_2 = 15.88 min (minor)]; $[\alpha]_D^{20}$ = + 8.8 (c = 0.50, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.26 – 7.23 (m, 2H), 7.18 – 7.13 (m, 2H), 6.18 (dd, *J* = 3.2, 2.0 Hz, 1H), 5.94 (d, *J* = 3.6 Hz, 1H), 5.13 – 5.07 (m, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.97 (dd, *J* = 12.0, 8.4 Hz, 1H), 3.64 (dd, *J* = 11.6, 10.0 Hz, 1H), 3.47 – 3.41 (m, 1H), 2.82 – 2.75 (m, 1H), 2.72 – 2.64 (m, 1H), 1.21 (t, *J* = 7.2 Hz, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 151.8, 142.1, 137.7, 128.9 (2C), 127.9, 127.3 (2C), 110.2, 107.1, 90.5, 61.2, 56.0, 49.0, 47.4, 34.5, 14.1;
IR (ATR): 3119, 2929, 1722, 1604, 1546, 1500, 1453, 1374, 1336, 1295, 1263, 1217, 1193, 1097, 1074, 1017, 924, 865, 803, 734, 698 cm^{-1};
HRMS (EI) m/z Calculated for $C_{18}H_{19}NO_5$ 329.1258, found 329.1260.

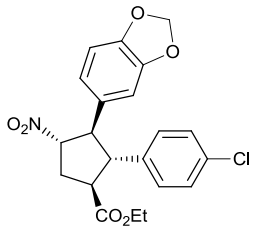


The compound **3f** was prepared according to the general procedure. The product was obtained as a colorless solid (80 mg, 42% yield); Melting point: 68-70 °C; Enantiomeric ratio was determined as 90:10 by HPLC [Chiralpak IC, elute: *n*-Heptan/*i*-PrOH = 97:3, detector: 214 nm, flow rate: 1.0 mL/min), 30 °C, t_1 = 12.52 min (minor), t_2 = 15.81 min (major)]; $[\alpha]_D^{20}$ = –15.4 (c = 0.50, $CHCl_3$);
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.21 – 7.17 (m, 1H), 7.16 – 7.14 (m, 2H), 6.67 – 6.62 (m, 2H), 6.54 (dd, *J* = 7.8, 2.4 Hz, 1H), 5.89 (s, 2H), 5.10 – 5.06 (m, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.78 (dd, J = 12.0, 7.8 Hz, 1H), 3.48 – 3.44 (m, 1H), 3.41 – 3.36 (m, 1H), 2.81 – 2.77 (m, 1H), 2.73 – 2.68 (m, 1H), 1.11 (t, *J* = 7.2 Hz, 3H);
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.3, 148.1, 147.2, 138.5, 131.4, 128.7 (2C), 127.5 (2C), 127.4, 121.1, 108.5, 107.3, 101.1, 91.2, 61.0, 58.8, 56.0, 49.8, 34.7, 14.0;
IR (ATR): 2977, 2898, 2782, 2321, 2103, 1721, 1611, 1544, 1491, 1442, 1372, 1244, 1182, 1100, 1032, 932, 864, 812, 759, 700 cm^{-1};
HRMS (EI) m/z Calculated for $C_{21}H_{21}NO_6$ 383.1363, found 383.1360.

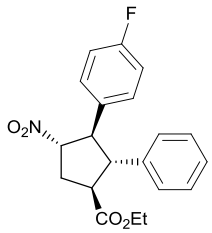


The compound **3g** was prepared according to the general procedure. The product was obtained as a colorless solid (65 mg, 40% yield); Melting point: 72-74 °C; Enantiomeric ratio was determined as 92.5:7.5 by HPLC (Chiralpak IA, elute: *n*-heptan/*i*-PrOH = 97:3, detector: 230 nm, flow rate: 0.7mL/min), 30 °C, t_1 = 13.04 min (minor), t_2 = 13.78 min (major); $[\alpha]_D^{20}$ = + 37.2 (c =0.50, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.30 – 7.16 (m, 5H), 6.19 (dd, *J* = 3.2, 2.0 Hz, 1H), 5.96 (d, *J* = 3.2 Hz, 1H), 5.27 – 5.17 (m, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 4.00 – 3.95 (m, 1H), 3.65 – 3.58 (m, 1H), 3.43 – 3.36 (m, 1H), 2.76 – 2.68 (m, 2H), 1.09 (t, *J* = 7.2 Hz, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 150.7, 142.5, 138.5, 128.7 (2C), 127.5, 127.4 (2C), 110.4, 107.8, 88.4, 61.0, 53.6, 52.1, 49.7, 34.9, 14.0;
IR (ATR): 3031, 2971, 1721, 1600, 1548, 1493, 1451, 1372, 1261, 1184, 1088, 1016, 920, 799, 742, 697 cm^{-1};
HRMS (EI) m/z Calculated for $C_{18}H_{19}NO_5$ 329.1258, found 329.1247.

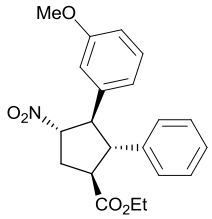


The compound **3h** was prepared according to the general procedure. The product was obtained as a yellowlish solid (107 mg, 51% yield); Melting point: 113-115°C; Enantiomeric ratio was determined as 93.5:6.5 by HPLC (Chiralpak IB, elute: *n*-Heptan:EtOH = 90/10, detector: 230 nm, flow rate: 0.5mL/min), 30 °C, t_1 = 16.27 min (minor), t_2 = 17.46 min (major); $[\alpha]_D^{20}$ = – 20.4 (c = 0.50, $CHCl_3$);
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.11 – 7.06 (m, 2H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.61 (d, *J* = 1.8 Hz, 1H), 6.52 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.91 (s, 2H), 5.08 – 5.04 (m, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.71 (dd, *J* = 12.0, 7.8 Hz, 1H), 3.44 – 3.41 (m, 1H), 3.37 – 3.32 (m, 1H), 2.81 - 2.76 (m, 1H), 2.72 – 2.67 (m, 1H), 1.13 (t, *J* = 7.2 Hz, 3H);
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0, 148.2, 147.3, 137.0, 133.2, 131.0, 128.9 (2C), 128.8 (2C), 121.1, 108.6, 107.2, 101.2, 91.0, 61.2, 58.9, 55.4, 49.6, 34.6, 14.1;
IR (ATR): 2943, 2898, 1720, 1611, 1545, 1490, 1443, 1369, 1314, 1279, 1248, 1213, 1178, 1093, 1040, 1014, 933, 844, 814, 721 cm^{-1};
HRMS (EI) m/z Calculated for $C_{21}H_{20}ClNO_6$ 417.0974, found 417.0982.



The compound **3i** was prepared according to the general procedure. The product was obtained as a colorless solid (32 mg, 18% yield); Melting point: 106-108 °C; Enantiomeric ratio was determined as 98:2 by HPLC (Chiralpak ID, elute: *n*-Heptan:EtOH = 97:3, detector: 214 nm, flow rate: 0.7 mL/min), 30 °C, t_1 = 16.16 min (minor), t_2 = 17.72 min (major); $[\alpha]_D^{20}$ = – 6.0 (c = 0.50, $CHCl_3$);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.22 – 7.19 (m, 1H), 7.15 – 7.11 (m, 2H), 7.10 – 7.06 (m, 2H), 6.97 – 6.91 (m, 2H), 5.13 - 5.09 (m, 1H), 4.07 (q, *J* = 7.2, 2H), 3.86 – 3.83 (m, 1H), 3.49 -3.39 (m, 2H), 2.86 - 2.80 (m, 1H), 2.76 – 2.71 (m, 1H), 1.11 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.3 , 162.2 (d, *J* = 244.5 Hz) , 138.3 , 133.4 (d, *J* = 4.5 Hz), 129.0 (d, J = 7.5 Hz, 2H), 128.7 (2C), 127.5 , 127.4 (2C) , 115.87 (d, *J* = 20 Hz, 2H) , 90.9 , 61.1 , 58.3 , 56.2 , 49.7 , 34.7 , 14.0 ;
IR (ATR): 3433, 2930, 2293, 2092, 1899, 1719, 1533, 1372, 1200, 1032, 803 cm^{-1};
HRMS (ESI) m/z Calculated for $C_{20}H_{20}FNO_4Na$[M+Na] 380.1269, found 380.1261.



The compound **3j** was prepared according to the general procedure. The product was obtained as a colorless solid (65 mg, 35% yield); Melting point: 64-66 °C; Enantiomeric ratio was determined as 93.5:6.5 by HPLC (Chiralpak IC, elute: *n*-Heptan:EtOH = 9:1, detector: 214 nm, flow rate: 0.5 mL/min), 30 °C, t_1 = 7.52 min (minor), t_2 = 8.53 min (major); $[\alpha]_D^{20}$ = – 8.4 (c = 0.50, $CHCl_3$);
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 7.21 – 7.14 (m, 4H), 6.76 – 6.70 (m, 2H), 6.64 – 6.60 (m, 1H), 5.17 – 5.13 (m, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.87 - 3.81 (m, 1H), 3.71 (s, 3H), 3.54 -3.50 (m, 1H), 3.44 – 3.40 (m, 1H), 2.84 – 2.78 (m, 1H), 2.76 – 2.70 (m, 1H), 1.11 (t, *J* = 7.2 Hz, 3H);
^{13}CNMR (150 MHz, $CDCl_3$) δ 173.2 , 159.8 , 139.5 , 138.5 , 129.9 , 128.6 (2C) , 127.5 (2C) , 127.4 , 119.5 , 113.4 , 112.9 , 91.0 , 61.0 , 58.8 , 56.1 , 55.1 , 49.9 , 35.0 , 14.1;
IR (ATR): 3444, 2940, 2286, 2076, 1921, 1723, 1552, 1462, 1366, 1188, 1044, 865, 767, 695 cm^{-1};
HRMS (ESI) m/z Calculated for $C_{21}H_{23}NO_5Na$ [M+Na] 392.1468, found 392.1457.

5. References

[1] a) N. E. Wurz, C. G. Daniliuc and F. Glorius, *Chem. Eur. J.*, 2012, **18**, 16297; b) H. U. Vora, S. P. Lathrop, N. T. Reynolds, M. S. Kerr, J. V. R. de Alaniz and T. Rovis, *Org. Synth.*, 2010, **87**, 350; c) J. R. Struble and J. W. Bode, *Org. Synth.*, 2010, **87**, 362; d) K. B. Ling and A. D. Smith, *Chem. Commun.*, 2011, **47**, 373.

[2] C.-L. Cao, Y.-Y. Zhou, J. Zhou, X.-L. Sun, Y. Tang, Y.-X. Li, G.-Y. Li and J. Sun, *Chem.-Eur. J.*, 2009, **15**, 11384.

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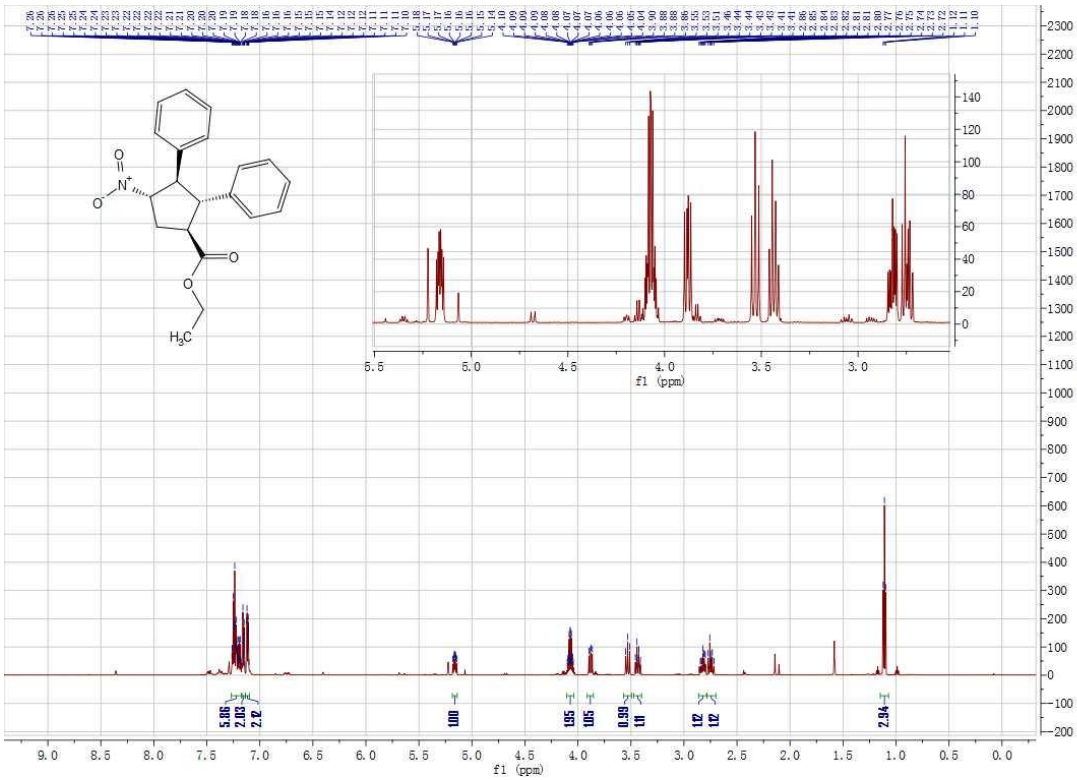
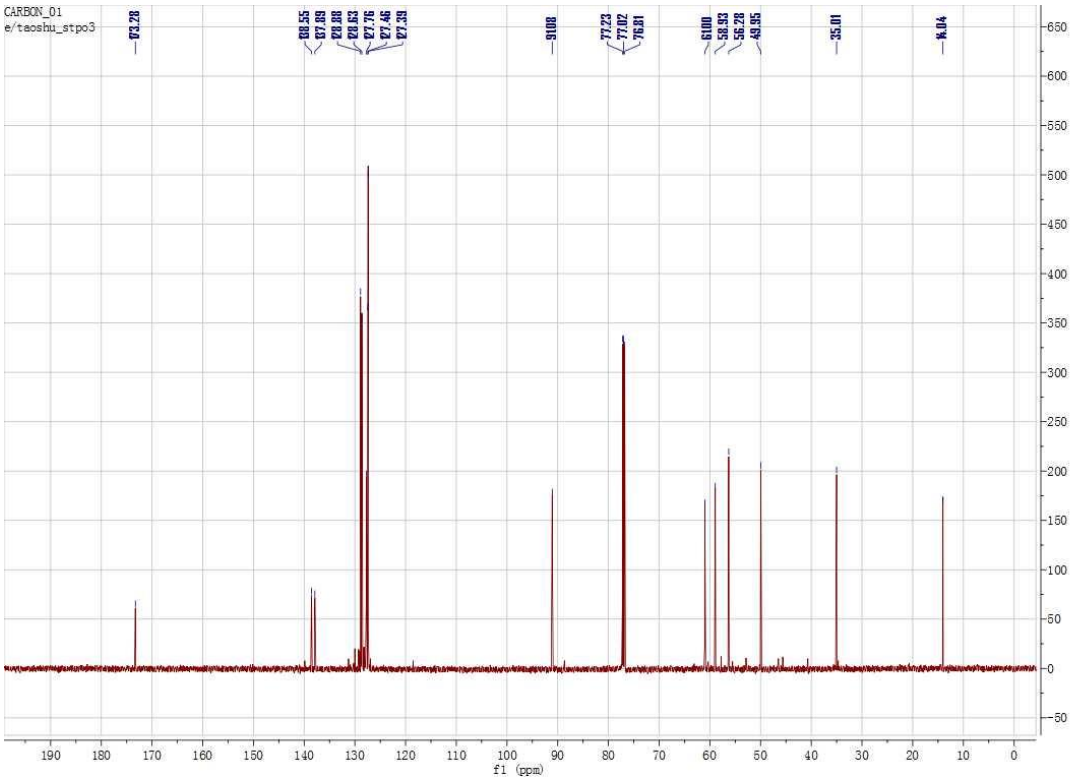
6. Copies of NMR spectra and HPLC measurements of the products 3

^{1}H NMR of **3a**



^{13}C NMR of **3a**



HPLC of **3a** (racemate)

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

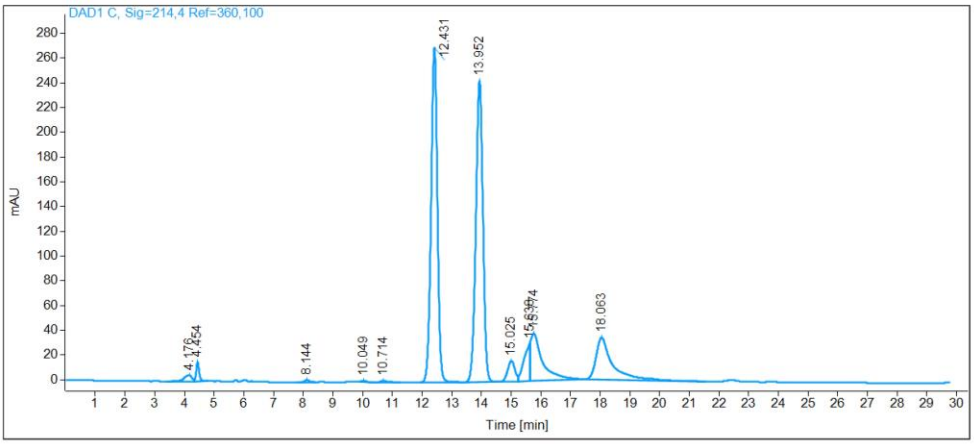
Sample name: ST PO3 rac

Data file: C:\SNOOPY\ST\ST PO3 RAC 2IA.D
Description: Laufmittel: n-Heptan/EtOH 97:3 Die Probe ist DCM/LM gelöst.

Injection date: 11/14/2014 8:41:53 AM
Acq. Analysis method: CHIRALPAKIARNP.M

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

Pressure at start: 34 bar **Start flow:** 0.700 ml/min **Column oven:** 29.99 °C



Name ST PO3 rac

RT [min]	Type	Area%	Area	Height	Width [min]
4.18	BV	0.78	88.22	4.83	0.28
4.45	VB	0.95	107.76	15.58	0.10
8.14	BB	0.16	18.77	1.78	0.16
10.05	BB	0.12	13.38	1.25	0.17
10.71	BB	0.23	25.96	1.54	0.24
12.43	BB	35.15	3999.49	270.45	0.23
13.95	BB	35.13	3996.74	243.78	0.25
15.02	BV	2.54	288.99	16.83	0.27
15.64	MF	3.58	407.49	30.42	0.22
15.77	FM	9.59	1090.98	38.32	0.47
18.06	BB	11.78	1339.93	34.18	0.55
	Sum	100.00	11377.72		

Agilent 1260 Infinity **Page 1**

Enantioenriched **3a**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

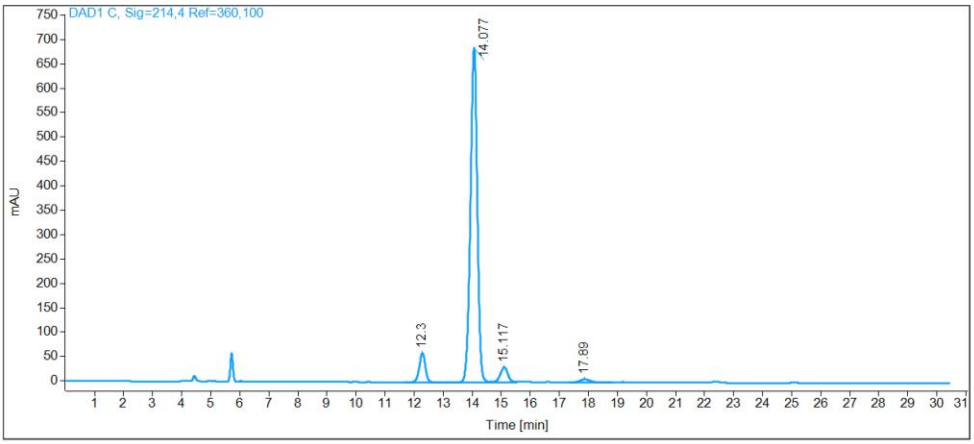
Sample name: **ST P 63**

Data file: C:\SNOOPY\ST\ST P 63 IA.D
Description: Laufmittel: n-Heptan/EtOH 97:3 ; Die Probe ist DCM/LM gelöst.

Injection date: 4/2/2015 8:38:23 AM
Acq. Analysis method: CHIRALPAKIARNP.M

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

Pressure at start: 31 bar **Start flow:** 0.700 ml/min **Column oven:** 30 °C

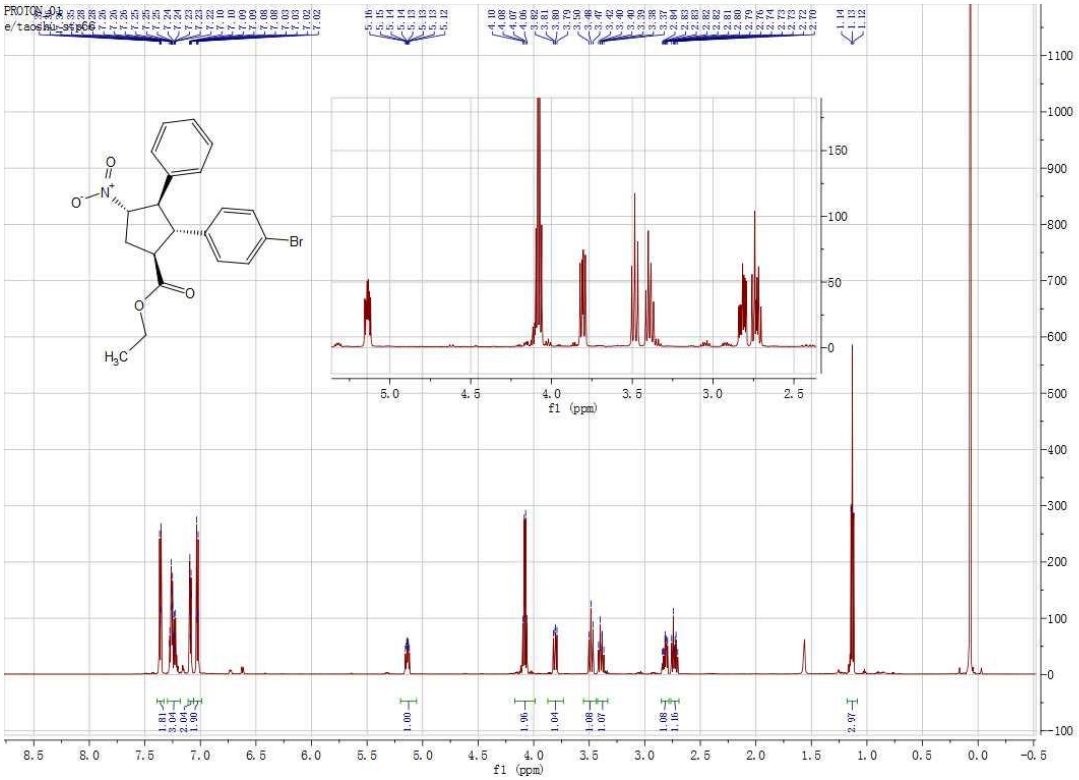


Name ST P 63

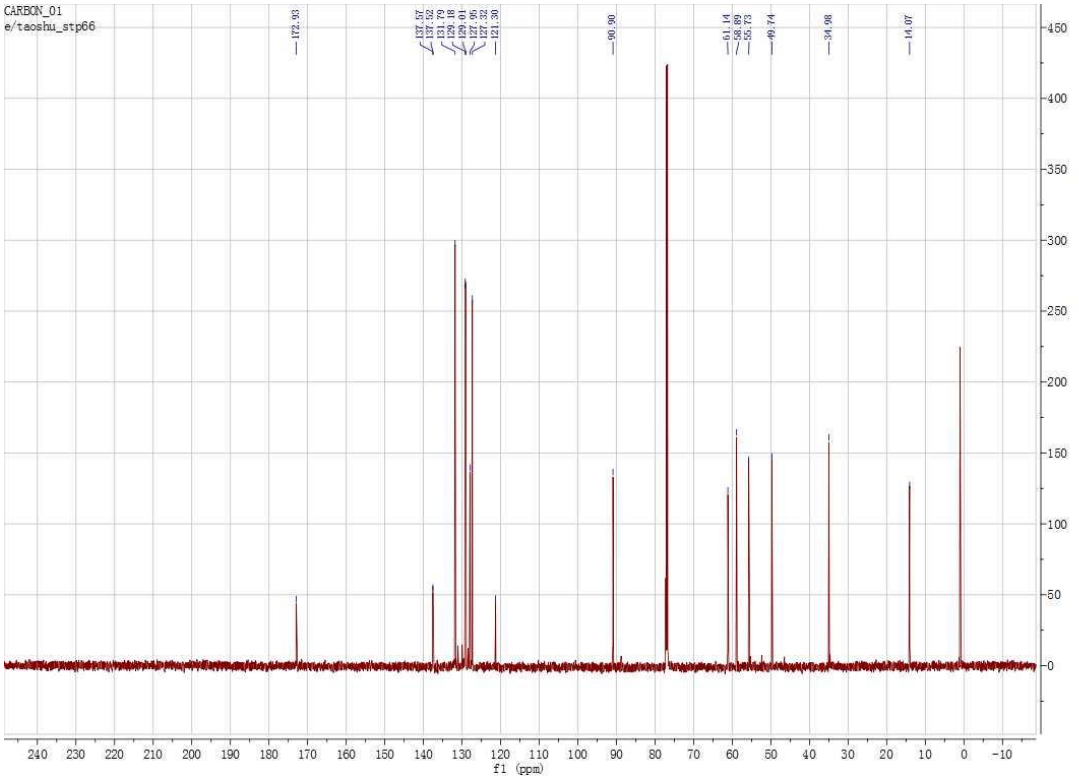
RT [min]	Type	Area%	Area	Height	Width [min]
12.30	BB	6.72	867.55	60.15	0.22
14.08	BV	87.47	11296.12	686.05	0.26
15.12	VV	4.44	572.78	30.90	0.28
17.89	BV	1.38	177.86	6.57	0.41
	Sum	100.00	12914.31		

Agilent 1260 Infinity **Page 1**

^{1}H NMR of **3b**



^{13}C NMR of **3b**



HPLC of **3b** (racemate)

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

Sample name: **ST P65 rac**

Data file: C:\SNOOPY\ST\P65RNXIA.D

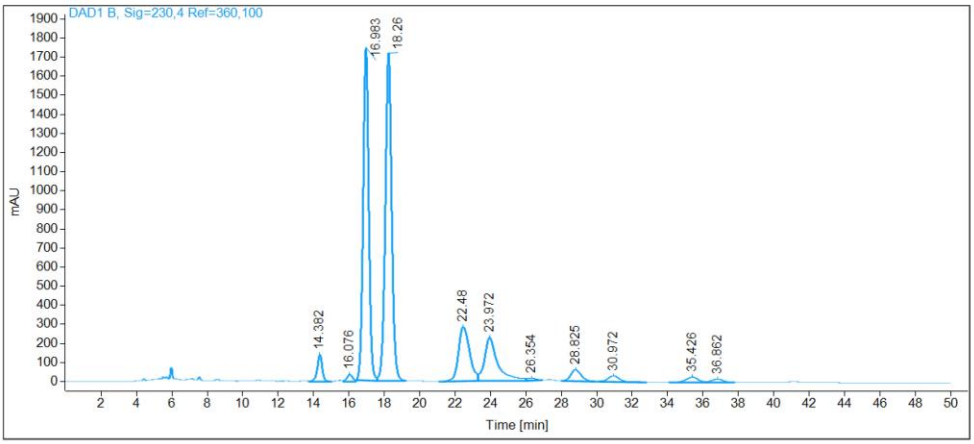
Description: Laufmittel: n-Heptan/iPrOH 97:3;
Probe ist in DCM/LM gelöst

Injection date: 12/3/2015 3:02:42 PM

Acq. Analysis method: CHIRALPAKIARNP.M

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

Pressure at start: 31 bar **Start flow:** 0.700 ml/min **Column oven:** 29.99 °C



Name ST P65 rac

RT [min]	Type	Area%	Area	Height	Width [min]
14.38	VB	2.30	2652.57	139.63	0.29
16.08	VV	0.65	752.33	35.29	0.33
16.98	MF	33.26	38277.40	1744.07	0.37
18.26	FM	37.50	43155.39	1718.52	0.42
22.48	BV	10.87	12505.05	285.44	0.69
23.97	VV	10.09	11608.42	226.67	0.73
26.35	VB	0.31	357.76	10.08	0.54
28.82	BV	2.11	2428.41	59.12	0.63
30.97	VB	1.18	1359.90	30.72	0.67
35.43	BV	1.10	1267.90	26.97	0.72
36.86	VB	0.63	727.41	17.06	0.66
	Sum	100.00	115092.54		

Agilent 1260 Infinity **Page 1**

Enantioenriched **3b**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

Sample name: **ST P66**

Data file: C:\SNOOPY\ST\P66RNXIA.D

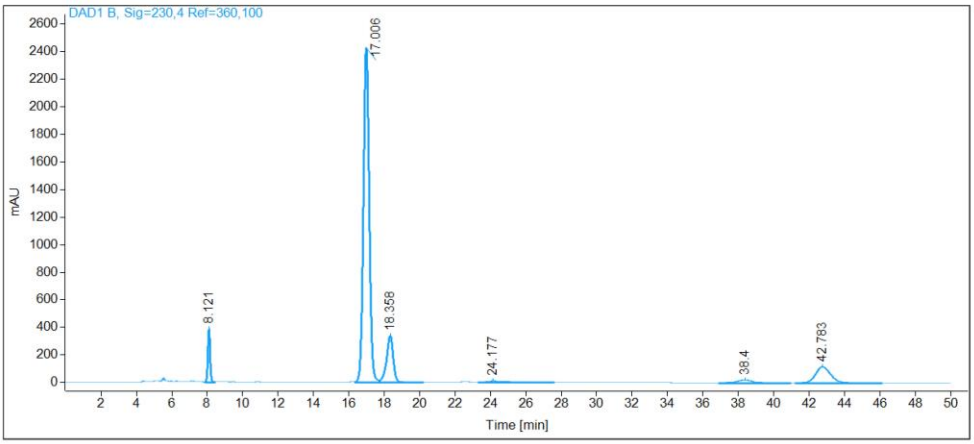
Description: Laufmittel: n-Heptan/iPrOH 97:3;
Probe ist in DCM/LM gelöst

Injection date: 12/3/2015 3:53:53 PM

Acq. Analysis method: CHIRALPAKIARNP.M

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

Pressure at start: 31 bar **Start flow:** 0.700 ml/min **Column oven:** 29.99 °C

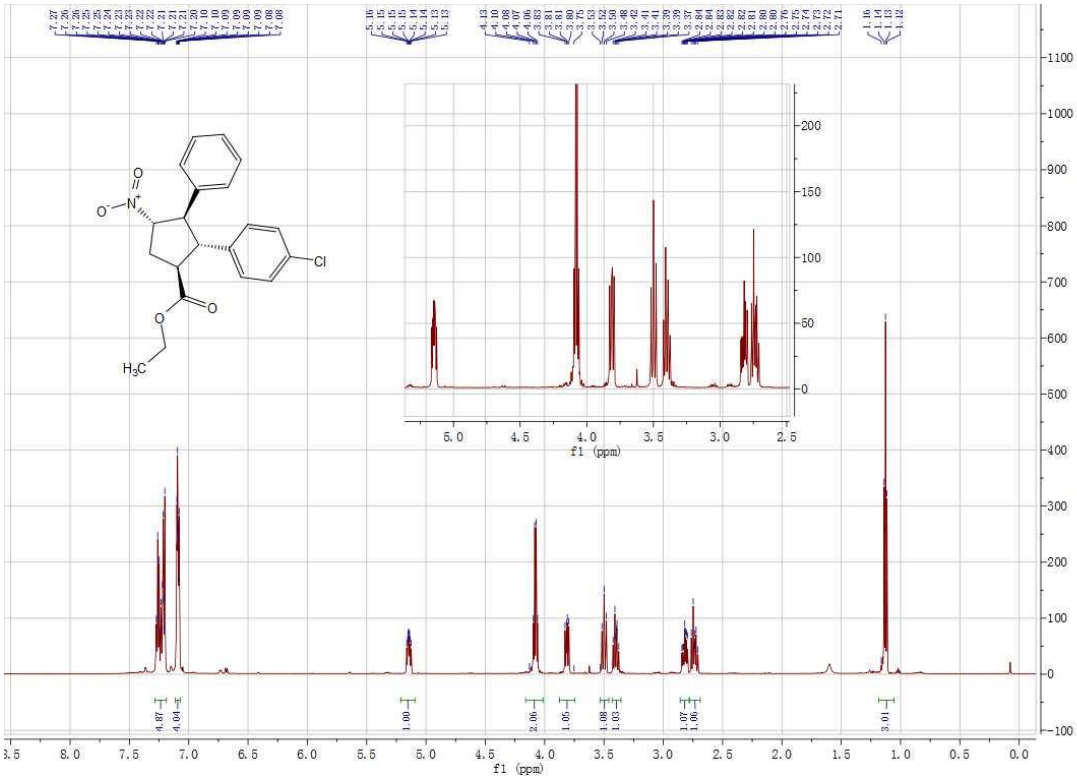


Name ST P66

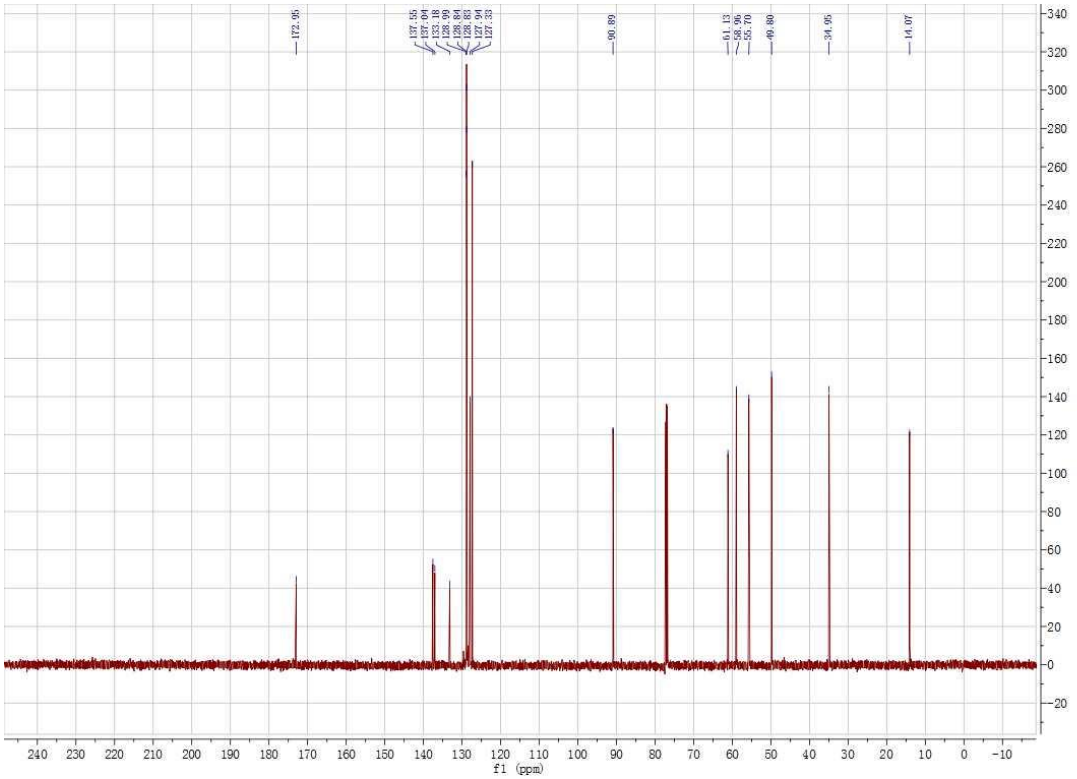
RT [min]	Type	Area%	Area	Height	Width [min]
8.12	BV	4.49	3412.46	386.34	0.14
17.01	VV	72.37	55014.02	2428.97	0.35
18.36	VB	11.60	8820.06	339.89	0.39
24.18	VB	0.93	703.58	9.82	0.98
38.40	BB	1.52	1156.51	21.64	0.81
42.78	BB	9.10	6914.34	117.48	0.90
	Sum	100.00	76020.98		

Agilent 1260 Infinity **Page 1**

^{1}H NMR of **3c**



^{13}C NMR of **3c**



HPLC of **3c** (racemate)

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

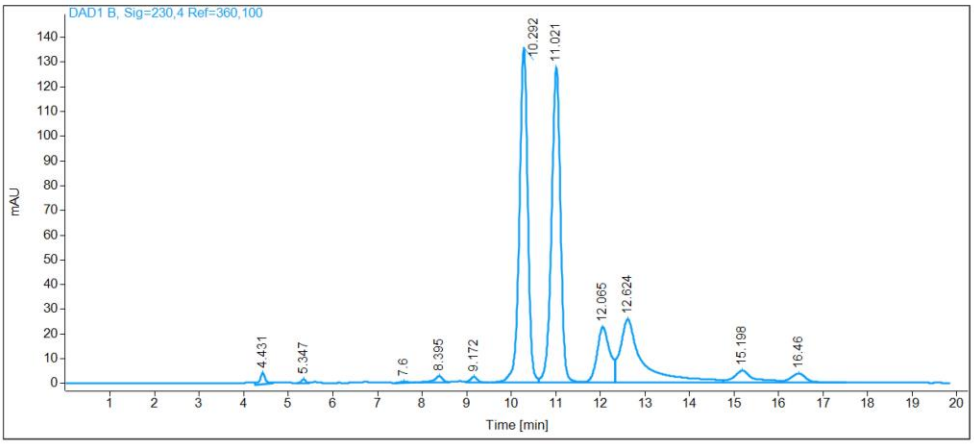
Sample name: **ST PO 30 rac**

Data file: C:\SNOOPY\ST\ST PO 30 RAC 3IA.D
Description: Laufmittel: n-Heptan/iPrOH 9:1 ; Die Probe ist DCM/LM gelöst.

Injection date: 12/15/2014 3:00:54 PM
Acq. Analysis method: CHIRALPAKIARNP.M

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

Pressure at start: 40 bar **Start flow:** 0.700 ml/min **Column oven:** 29.99 °C



Name ST PO 30 rac

RT [min]	Type	Area%	Area	Height	Width [min]
4.43	MM	0.73	37.75	4.55	0.14
5.35	BV	0.17	9.04	1.48	0.10
7.60	BB	0.12	6.10	0.45	0.21
8.39	BB	0.63	32.64	2.51	0.19
9.17	VB	0.45	23.53	2.22	0.16
10.29	BV	34.12	1770.03	135.50	0.20
11.02	VB	33.94	1760.35	127.43	0.21
12.07	BV	8.39	435.48	22.29	0.29
12.62	VV	16.94	878.86	25.45	0.47
15.20	VV	2.82	146.45	4.77	0.43
16.46	VB	1.68	87.17	3.61	0.36
	Sum	100.00	5187.42		

Agilent 1260 Infinity **Page 1**

Enantioenriched **3c**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

Sample name: **ST P73**

Data file: C:\SNOOPY\ST\P73NIA.D

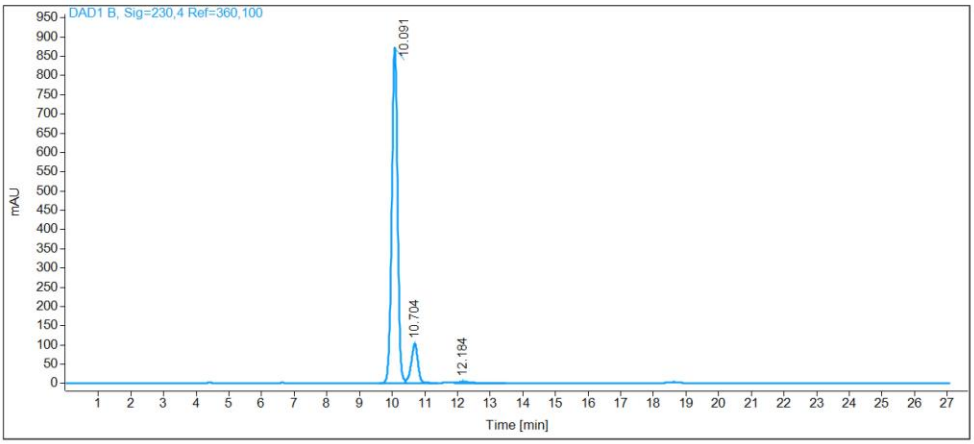
Description: Laufmittel: n-Heptan/iPrOH 9:1;
Probe ist in DCM/LM gelöst

Injection date: 12/15/2015 1:57:47 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

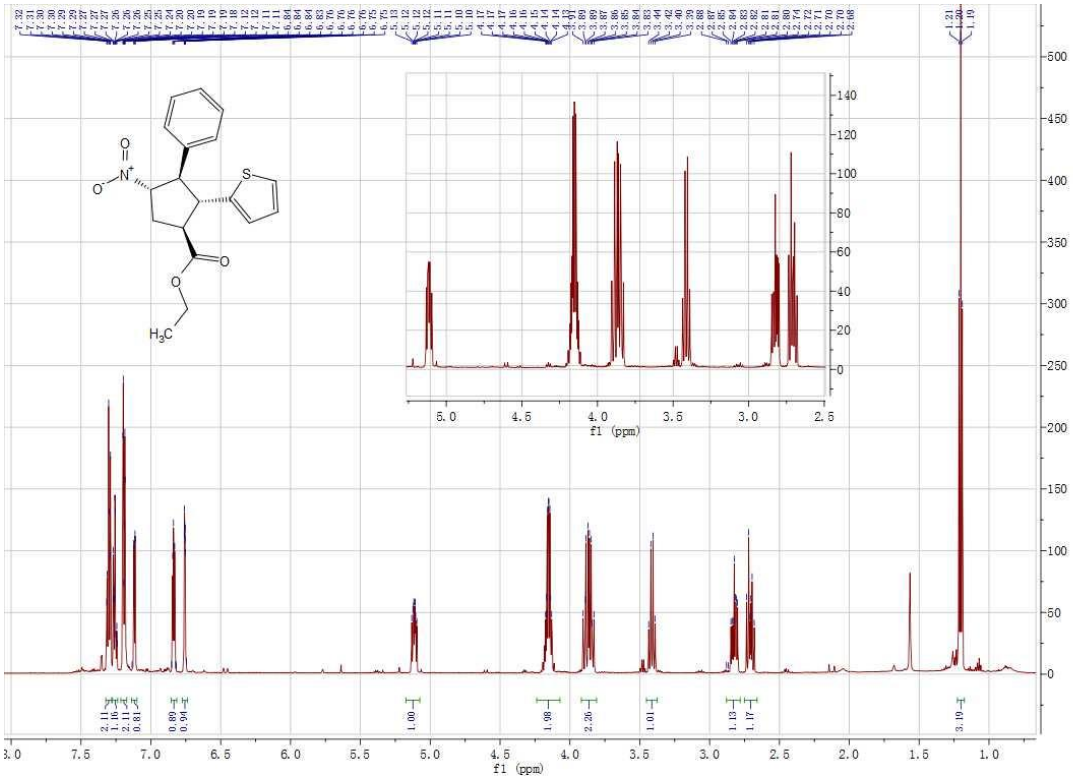


Name ST P73

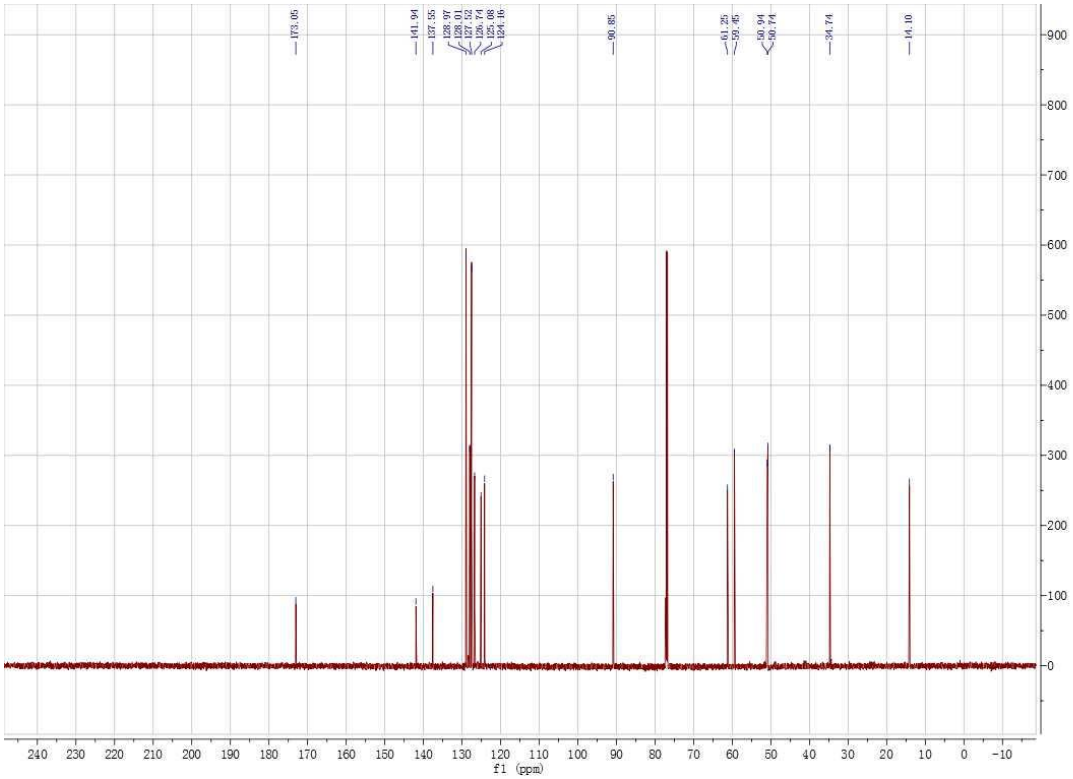
RT [min]	Type	Area%	Area	Height	Width [min]
10.09	BV	87.57	10751.54	871.49	0.19
10.70	VB	11.69	1435.80	101.93	0.22
12.18	VB	0.74	90.58	4.07	0.32
	Sum	100.00	12277.92		

Agilent 1260 Infinity **Page 1**

^{1}H NMR of **3d**



^{13}C NMR of **3d**



HPLC of **3d**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

Sample name: **ST P 85 rac**

Data file: C:\SNOOPY\ST\P85RIC.D

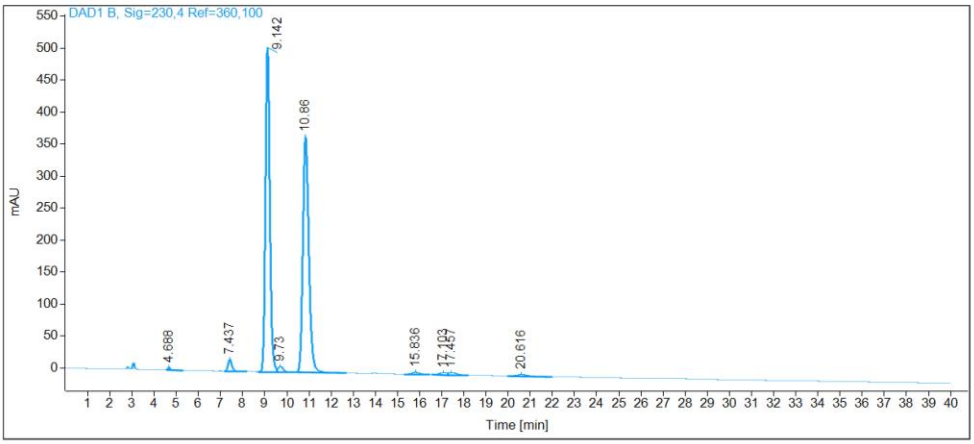
Description: Laufmittel: n-Heptan/iPrOH 97:3;
Probe ist in LM/DCM gelöst

Injection date: 7/9/2015 4:57:02 PM

Acq. Analysis method: CHIRALPAKIC1-6LNP.M

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

Pressure at start: 25 bar **Start flow:** 0.700 ml/min **Column oven:** 29.98 °C



Name ST P 85 rac

RT [min]	Type	Area%	Area	Height	Width [min]
4.69	BB	0.19	28.14	4.29	0.10
7.44	VB	1.49	219.65	18.29	0.18
9.14	BV	47.62	7002.45	506.94	0.21
9.73	VV	0.99	145.82	8.99	0.24
10.86	VB	47.12	6928.46	367.96	0.29
15.84	BB	0.56	82.59	3.29	0.39
17.10	BV	0.62	91.14	3.63	0.38
17.46	VB	0.69	100.81	3.70	0.42
20.62	BB	0.71	104.55	2.82	0.56
	Sum	100.00	14703.62		

Agilent 1260 Infinity **Page 1**

Enantioenriched **3d**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

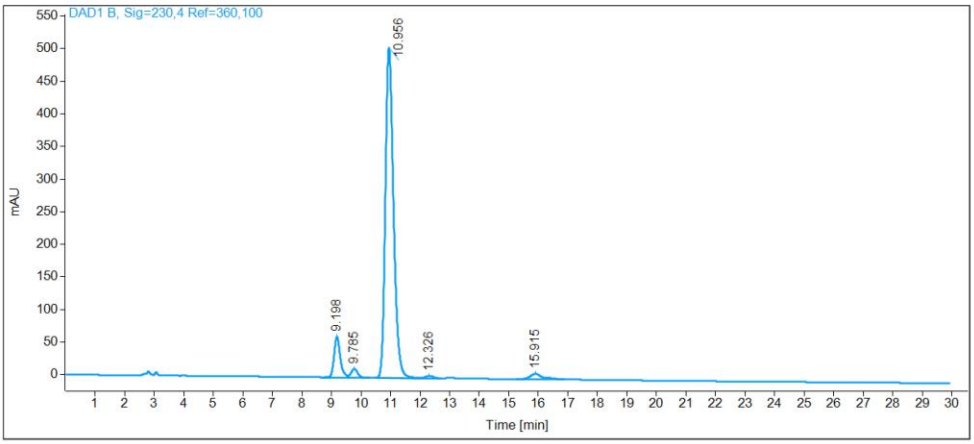
Sample name: **ST P 84**

Data file: C:\SNOOPY\ST\ST P 84 IC.D
Description: Laufmittel: n-Heptan/iPrOH 97:3; Die Probe ist DCM/LM gelöst.

Injection date: 7/10/2015 8:15:02 AM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

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

Pressure at start: 25 bar **Start flow:** 0.700 ml/min **Column oven:** 29.99 °C

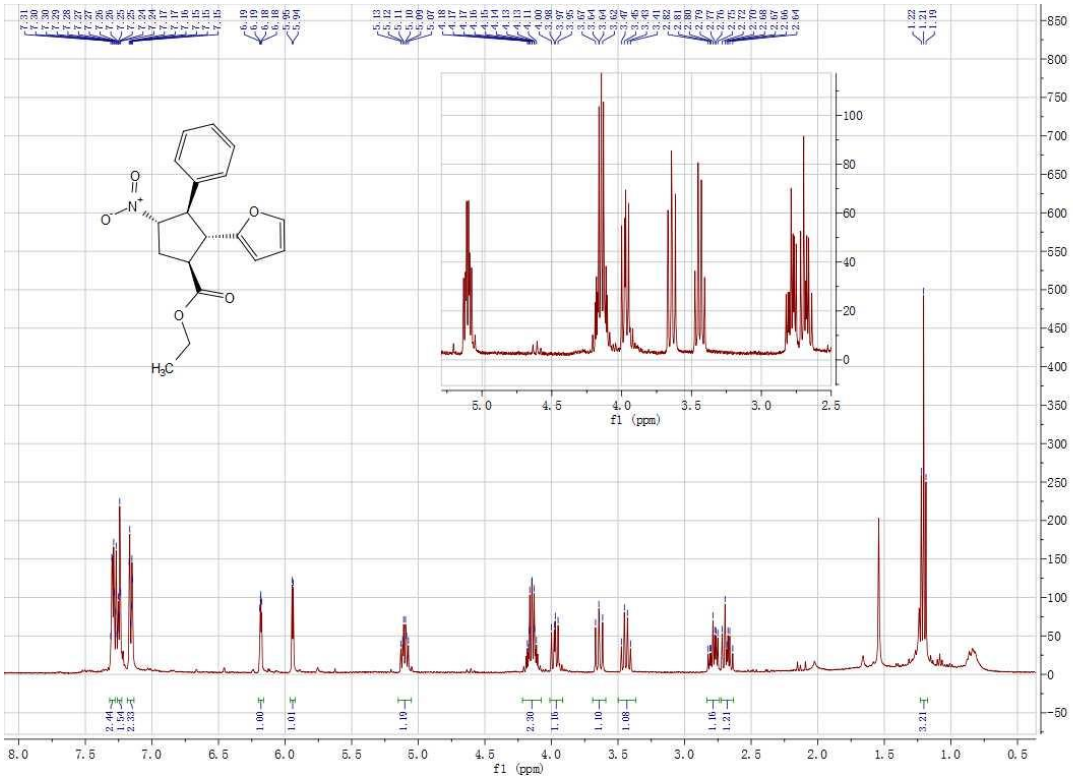


Name ST P 84

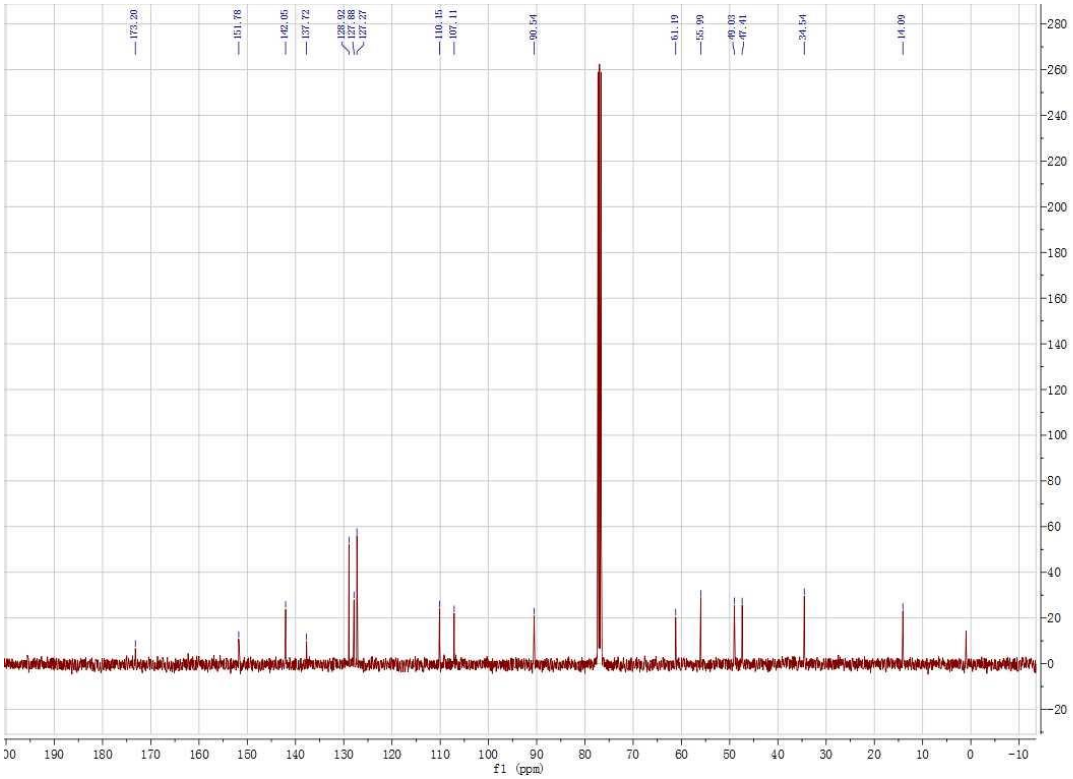
RT [min]	Type	Area%	Area	Height	Width [min]
9.20	BV	8.13	903.73	62.26	0.22
9.78	VB	1.88	208.83	13.60	0.24
10.96	BV	86.98	9666.20	506.60	0.29
12.33	VV	0.71	78.50	4.01	0.29
15.92	BB	2.30	255.46	8.39	0.45
	Sum	100.00	11112.72		

Agilent 1260 Infinity **Page 1**

^{1}H NMR of **3e**



^{13}C NMR of **3e**



HPLC of **3e** (racemate)

AK Enders - Analytische HPLC

Agilent Technologies

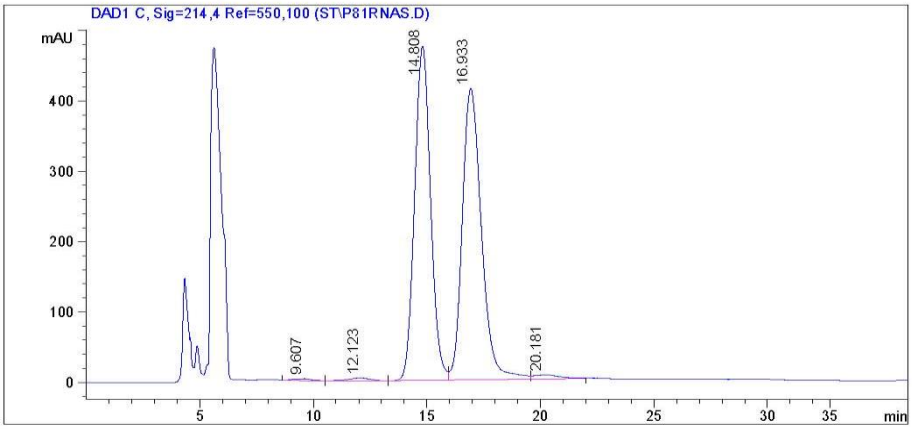
Sample Name: ST P 81 rac
Data file: D:\ERNIE\ST\P81RNAS.D
Sample Info: Mobile phase: n-Heptane/iPrOH 97:3;
The sample is solved in DCM/LM

Column: DAICELAS.M
Column info: Chiralpak AS (250 x 4.6)mm 10µ

Operator: Analytical Lab AKEN

Injektion Time: 09:55:21
Injektion Date: 15.12.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	23.0	22.0
Flow in ml/min:	0.7	0.7



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	9.61	0.66	2.73	149.16	0.31
2	12.12	0.78	3.86	251.25	0.52
3	14.81	0.76	474.74	23193.73	47.94
4	16.93	0.90	413.85	24296.00	50.22
5	20.18	1.00	5.77	489.18	1.01
Total				48379.33	100.00

Enantioenriched **3e**

AK Enders - Analytische HPLC

Agilent Technologies

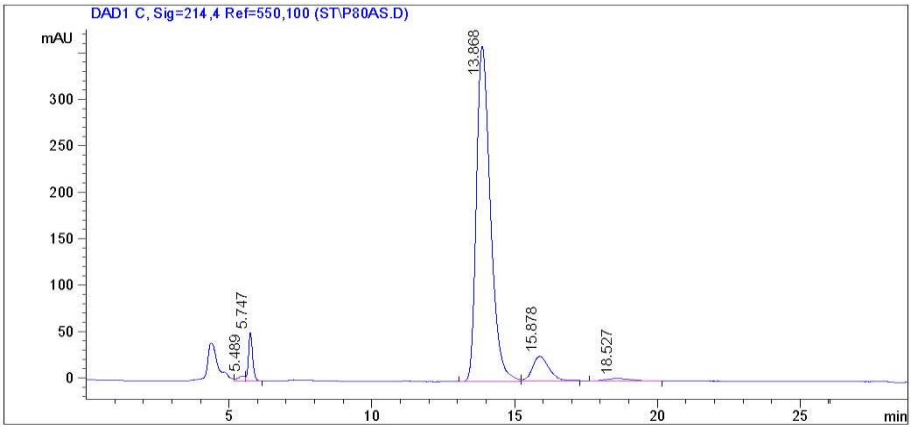
Sample Name: ST P 80
Data file: D:\ERNIE\ST\P80AS.D
Sample Info: Laufmittel: n-Heptan/iPrOH 97:3;
Die Probe ist in DCM/LM gelöst

Säule: DAICELAS.M
Säuleninfo: Chiralpak AS (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

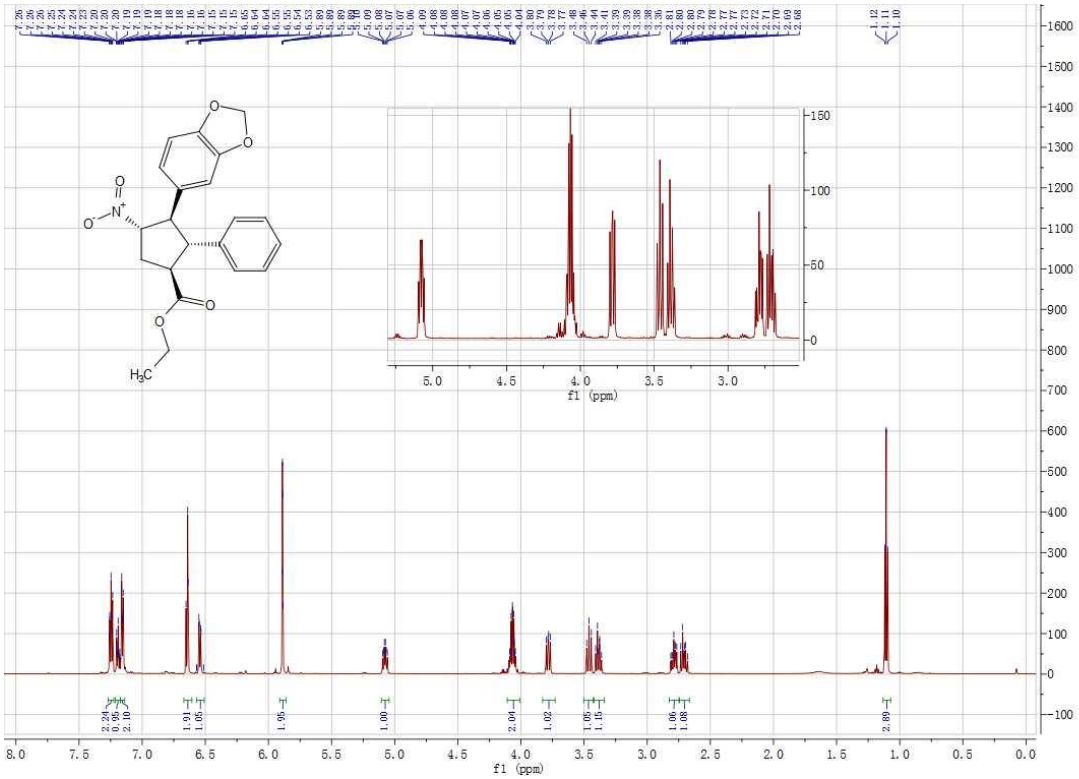
Injektion Time: 08:33:56
Injektion Date: 08.07.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	22.6	22.8
Flow in ml/min:	0.7	0.7

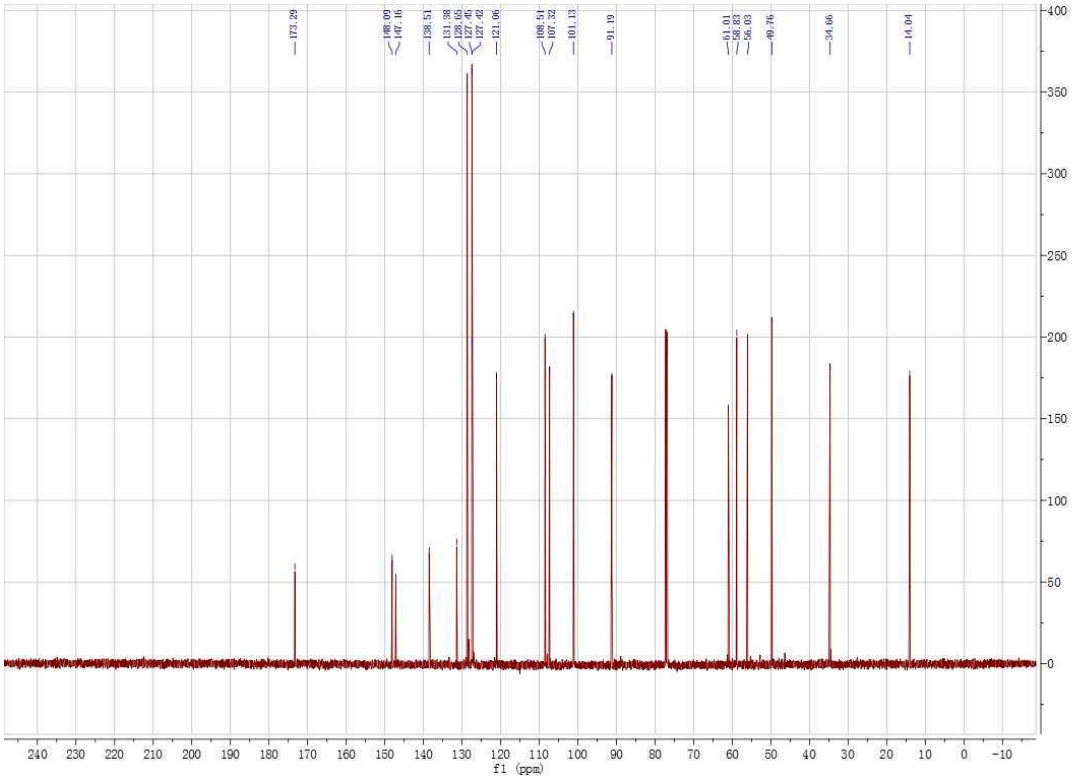


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.49	0.25	5.52	93.67	0.66
2	5.75	0.15	51.69	512.20	3.63
3	13.87	0.52	360.76	12272.46	86.99
4	15.88	0.60	26.75	1066.69	7.56
5	18.53	0.76	2.55	163.05	1.16
Total				14108.08	100.00

^{1}H NMR **3f**



^{13}C NMR of **3f**



HPLC of **3f** (racemate)

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

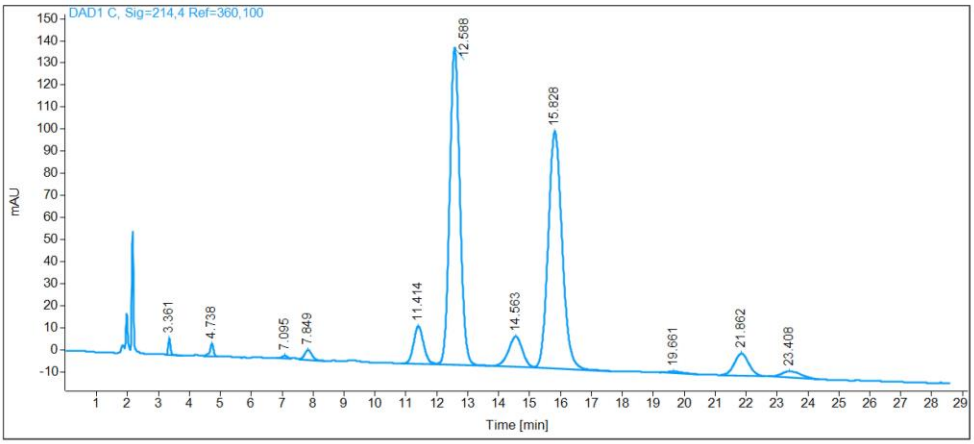
Sample name: **ST P 71 rac**

Data file: C:\SNOOPY\ST\ST P 71 RAC N3IC.D
Description: Laufmittel: n-Heptan/iPrOH 97:3; Die Probe ist DCM/LM gelöst.

Injection date: 7/6/2015 1:05:59 PM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

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

Pressure at start: 36 bar **Start flow:** 1.000 ml/min **Column oven:** 30 °C



Name ST P 71 rac

RT [min]	Type	Area%	Area	Height	Width [min]
3.36	VB	0.48	39.16	7.53	0.08
4.74	VV	0.60	49.01	5.91	0.12
7.09	BV	0.21	16.79	1.24	0.20
7.85	VB	0.91	74.46	4.52	0.25
11.41	BV	4.76	387.84	17.13	0.35
12.59	VB	40.53	3303.27	143.74	0.36
14.56	BV	5.35	435.89	13.88	0.47
15.83	VB	41.24	3361.28	107.42	0.48
19.66	BB	0.33	27.29	0.77	0.43
21.86	BB	4.02	327.42	10.01	0.50
23.41	BB	1.57	127.59	2.85	0.57
	Sum	100.00	8149.99		

Agilent 1260 Infinity **Page 1**

Enantioenriched **3f**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

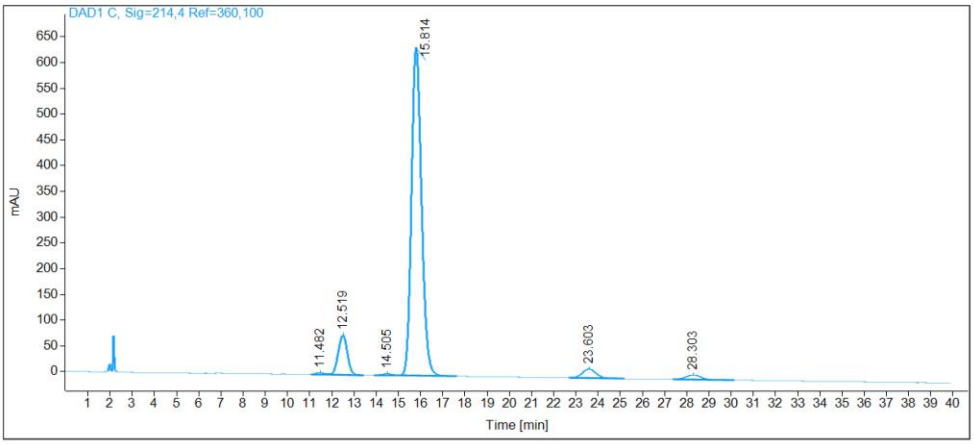
Sample name: **ST P 72**

Data file: C:\SNOOPY\ST\ST P 72 N1IC.D
Description: Laufmittel: n-Heptan/iPrOH 97:3; Die Probe ist DCM/LM gelöst.

Injection date: 7/6/2015 1:39:12 PM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

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

Pressure at start: 36 bar **Start flow:** 1.000 ml/min **Column oven:** 30.01 °C

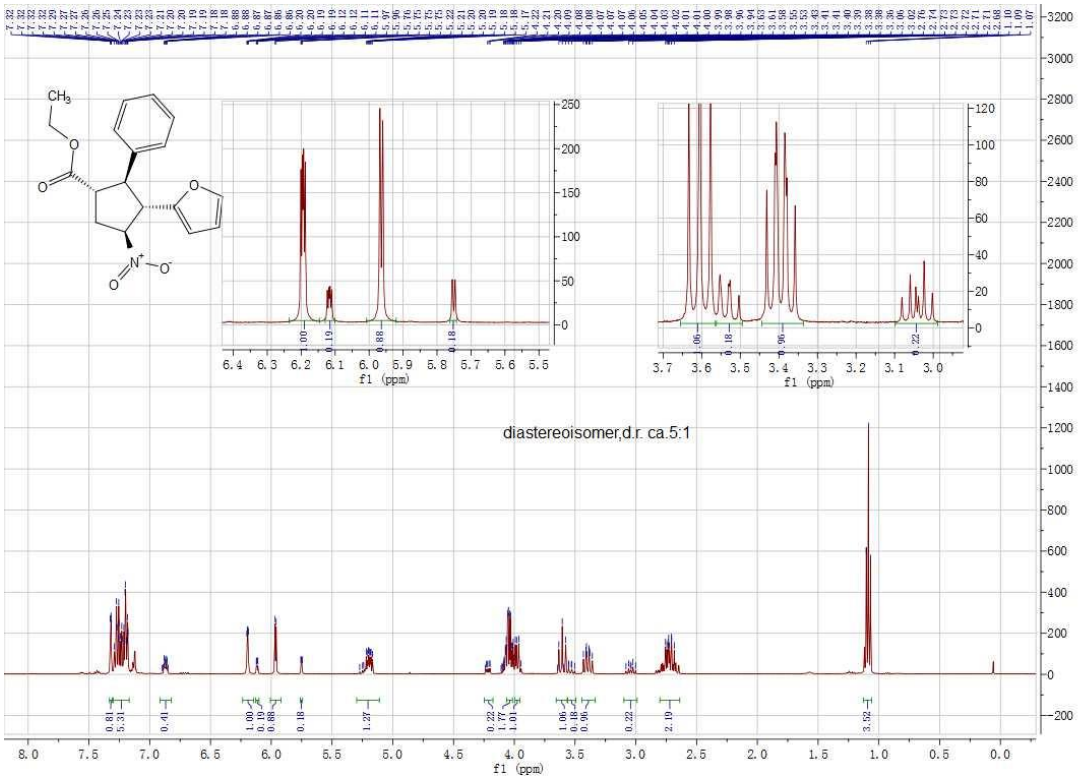


Name ST P 72

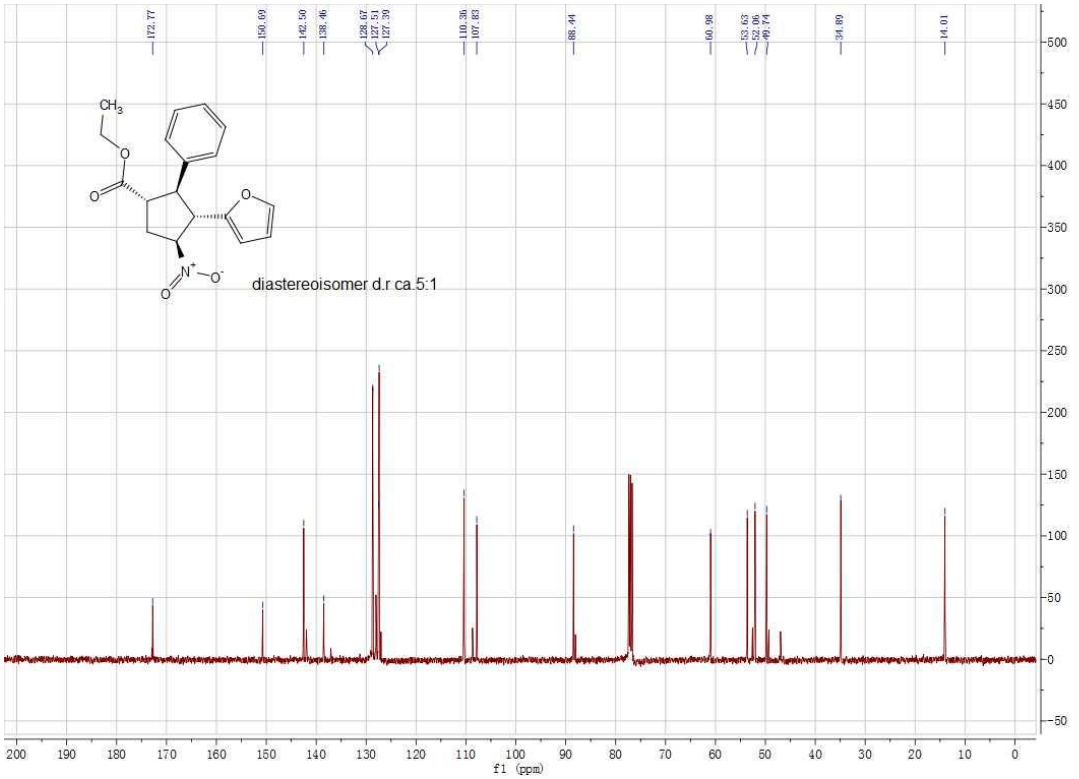
RT [min]	Type	Area%	Area	Height	Width [min]
11.48	BV	0.42	99.35	3.82	0.39
12.52	VB	9.30	2199.84	76.60	0.46
14.51	BV	0.39	91.51	2.96	0.43
15.81	VB	84.77	20050.56	636.95	0.49
23.60	BB	3.32	785.95	17.89	0.67
28.30	BB	1.80	424.76	9.16	0.70
	Sum	100.00	23651.95		

Agilent 1260 Infinity **Page 1**

^{1}H NMR of **3g**



^{13}C NMR of **3g**



HPLC of **3g** (racemate)

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

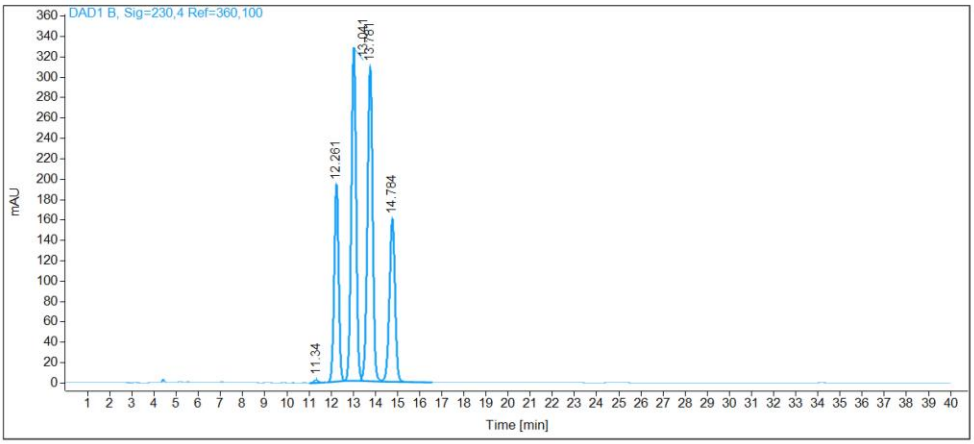
Sample name: **ST P 69 rac**

Data file: C:\SNOOPY\ST\ST P 69 RAC IA.D
Description: Laufmittel: n-Heptan/iPrOH 97:3 ; Die Probe ist DCM/LM gelöst.

Injection date: 4/24/2015 9:50:20 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:** 30.01 °C



Name ST P 69 rac

RT [min]	Type	Area%	Area	Height	Width [min]
11.34	BB	0.24	37.49	2.73	0.21
12.26	BB	17.49	2740.09	193.47	0.22
13.04	BV	31.96	5007.15	327.04	0.24
13.78	VV	32.39	5073.62	309.05	0.26
14.78	VB	17.92	2807.24	159.72	0.27
	Sum	100.00	15665.60		

Agilent 1260 Infinity **Page 1**

Enantioenriched **3g**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

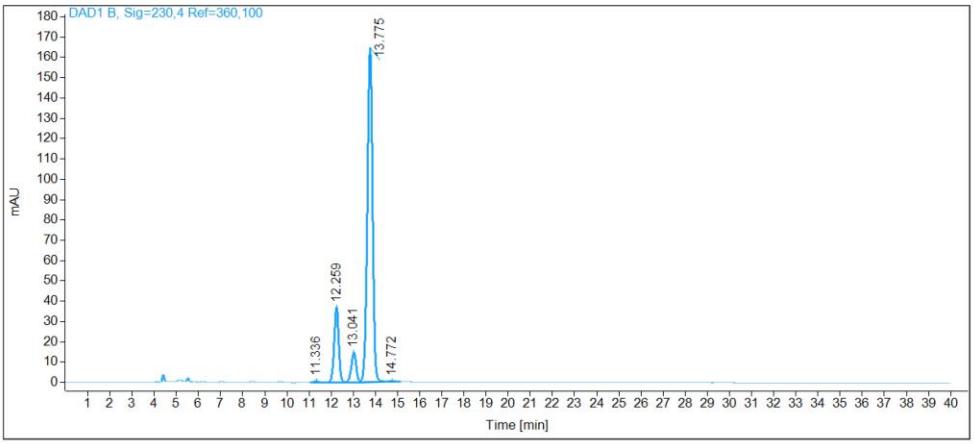
Sample name: **ST P 70**

Data file: C:\SNOOPY\ST\ST P 70 IA.D
Description: Laufmittel: n-Heptan/iPrOH 97:3 ; Die Probe ist DCM/LM gelöst.

Injection date: 4/24/2015 10:40:21 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:** 30 °C

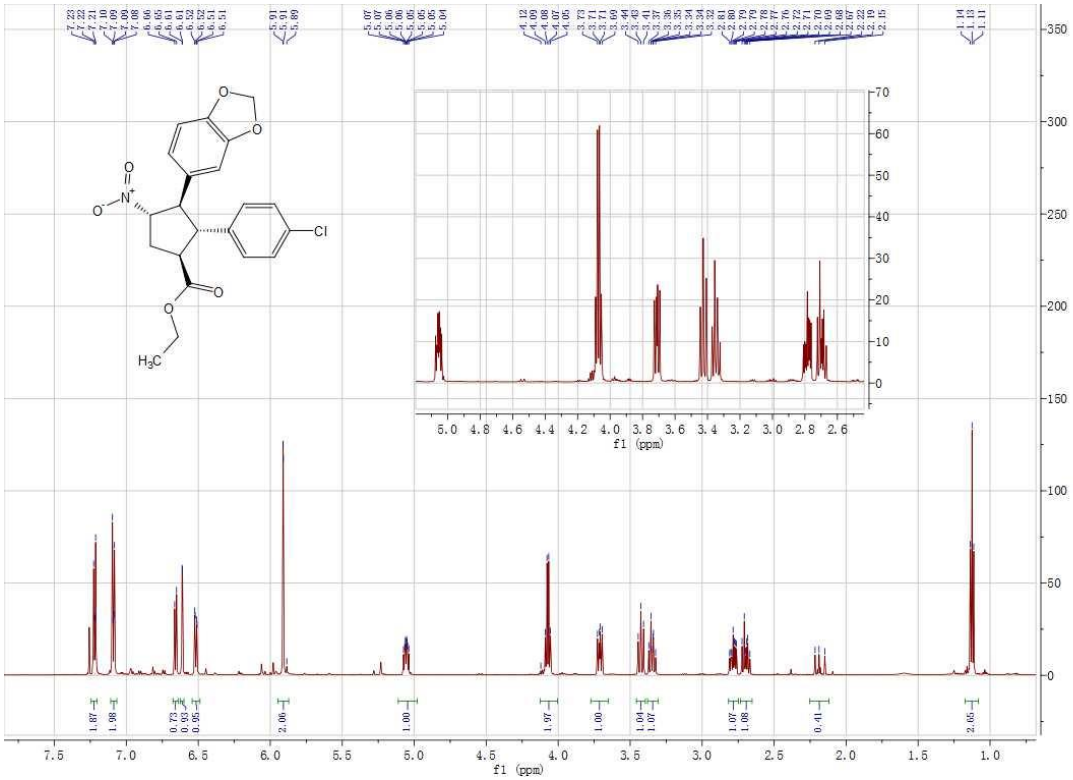


Name ST P 70

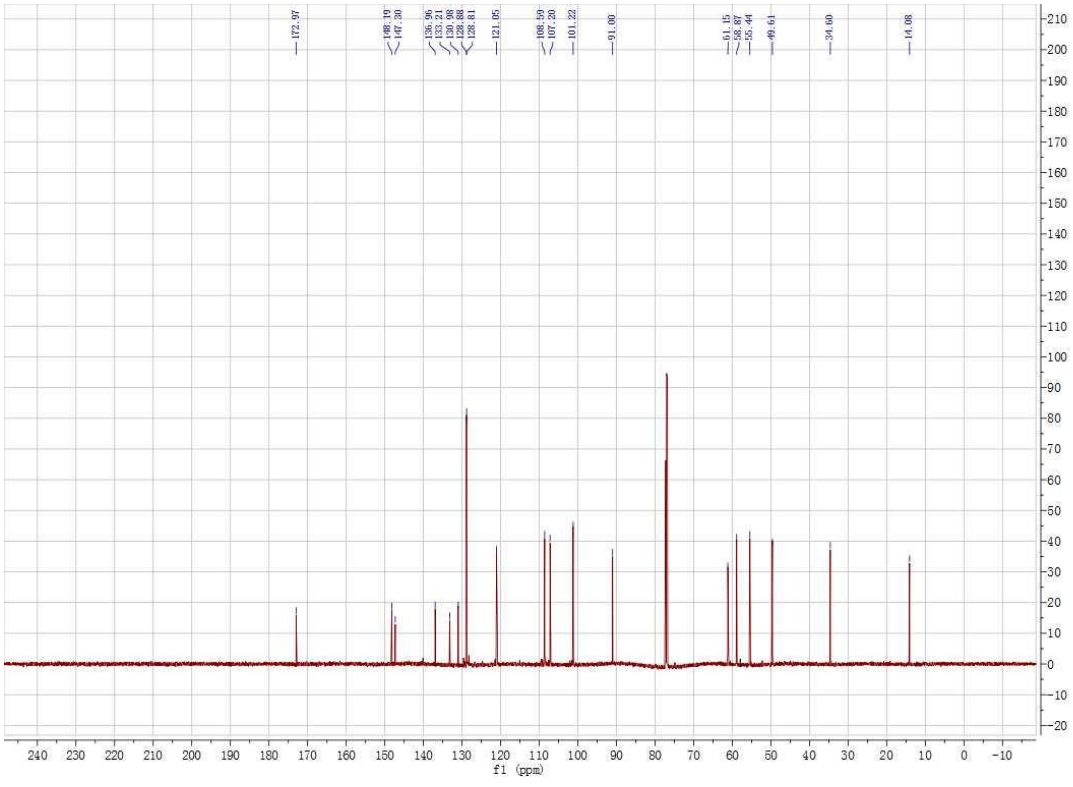
RT [min]	Type	Area%	Area	Height	Width [min]
11.34	VB	0.42	14.58	0.91	0.23
12.26	BB	15.10	522.05	36.76	0.22
13.04	BV	6.29	217.27	14.43	0.23
13.77	VV	77.82	2690.04	164.53	0.25
14.77	VB	0.37	12.91	0.66	0.29
	Sum	100.00	3456.84		

Agilent 1260 Infinity **Page 1**

^{1}H NMR of **3h**



^{13}C NMR of **3h**



HPLC of **3h** (racemate)

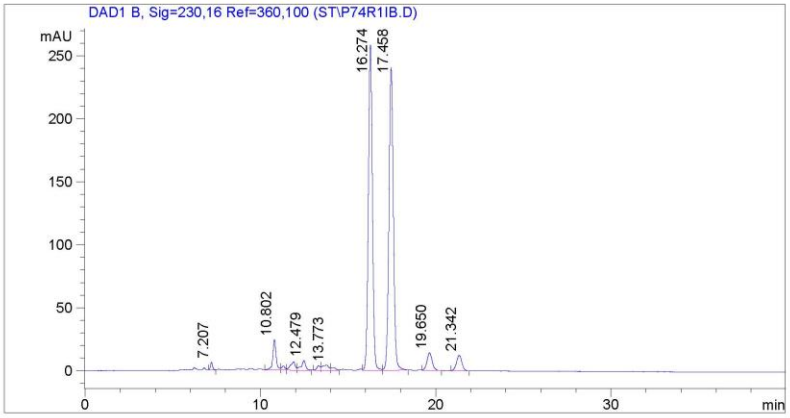
AK Enders - Analytische HPLC

Sample Name: ST P 74 rac
Data file: D:\GONZO\ST\P74R1IB.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst

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

Injektion Time: 16:49:11
Injektion Date: 01.06.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	24.1	24.0
Flow in ml/min:	0.50	0.50



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	7.21	0.13	6.42	56.39	0.57
2	10.80	0.20	24.18	326.69	3.33
3	11.31	0.21	3.40	47.23	0.48
4	11.89	0.27	6.65	131.00	1.34
5	12.48	0.25	7.74	137.67	1.40
6	13.32	0.21	3.61	50.45	0.51
7	13.77	0.34	4.13	105.48	1.08
8	14.18	0.26	2.11	38.51	0.39
9	16.27	0.25	258.21	4148.20	42.28
10	17.46	0.27	240.23	4219.65	43.01
11	19.65	0.31	13.99	287.00	2.93
12	21.34	0.33	12.34	262.30	2.67
Total				9810.57	100.00

Enantioenriched **3h**

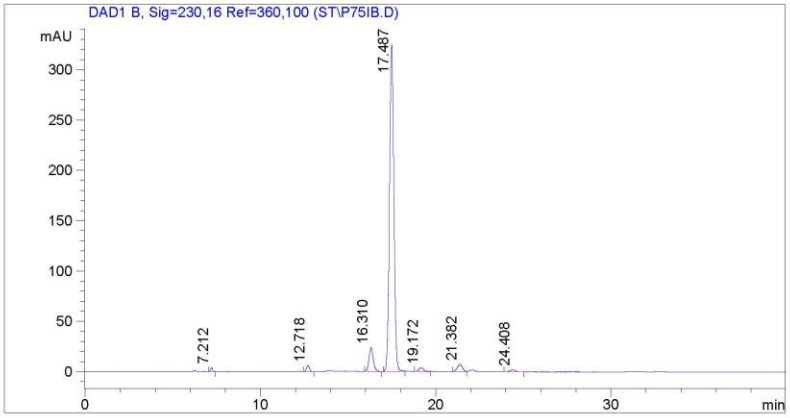
AK Enders - Analytische HPLC

Sample Name: ST P 75
Data file: D:\GONZO\ST\P75IB.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst

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

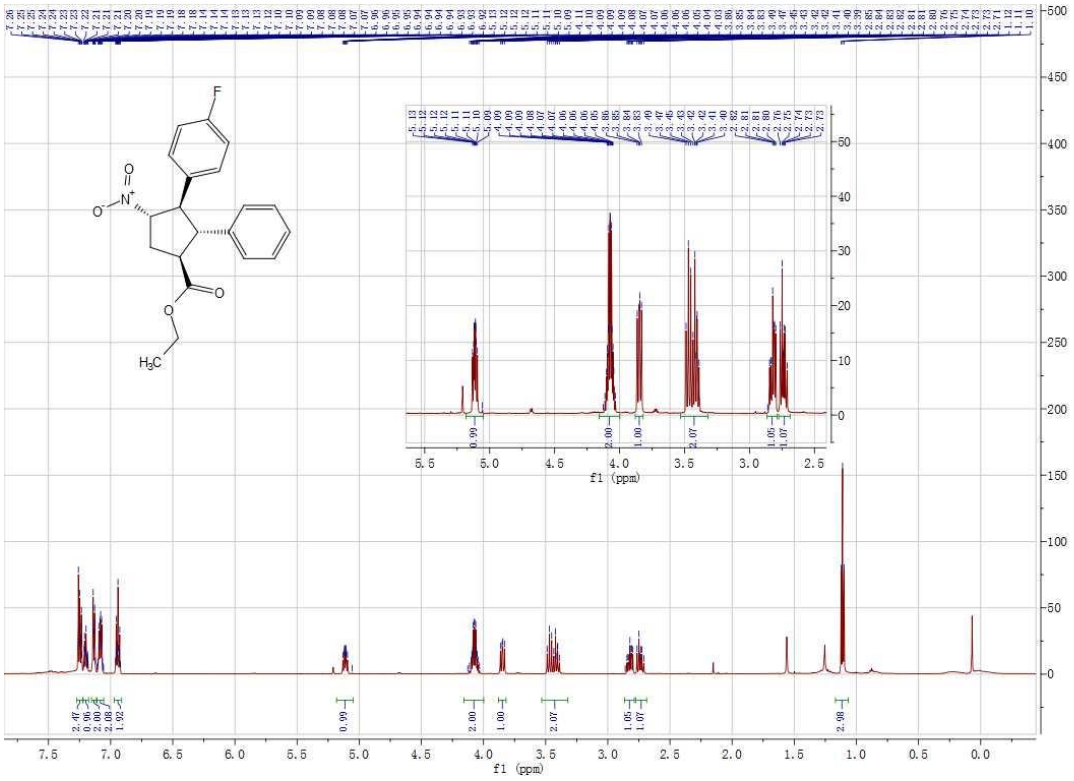
Injektion Time: 17:30:24
Injektion Date: 01.06.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	23.7	23.9
Flow in ml/min:	0.50	0.50

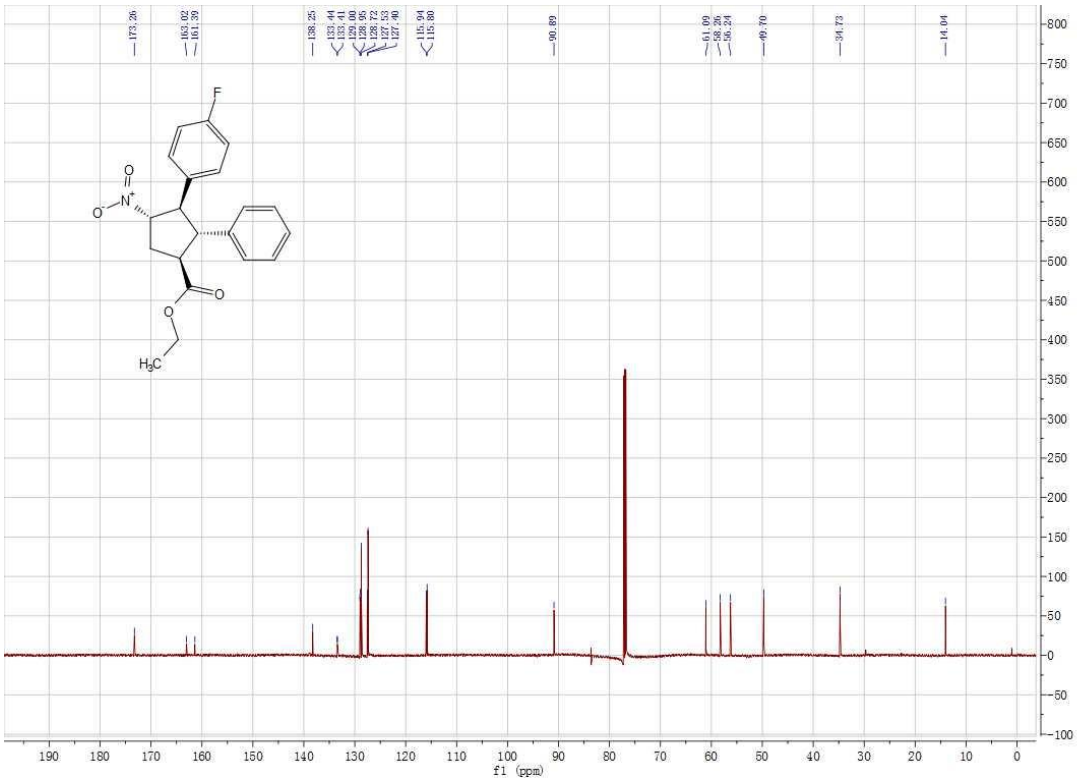


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	7.21	0.12	3.97	30.60	0.48
2	12.72	0.19	6.28	76.42	1.19
3	16.31	0.26	23.88	406.20	6.35
4	17.49	0.27	324.42	5613.50	87.78
5	19.17	0.29	3.78	71.73	1.12
6	21.38	0.32	7.18	149.64	2.34
7	24.41	0.34	1.95	46.83	0.73
Total				6394.91	100.00

^{1}H NMR of **3i**



^{13}C NMR of **3j**

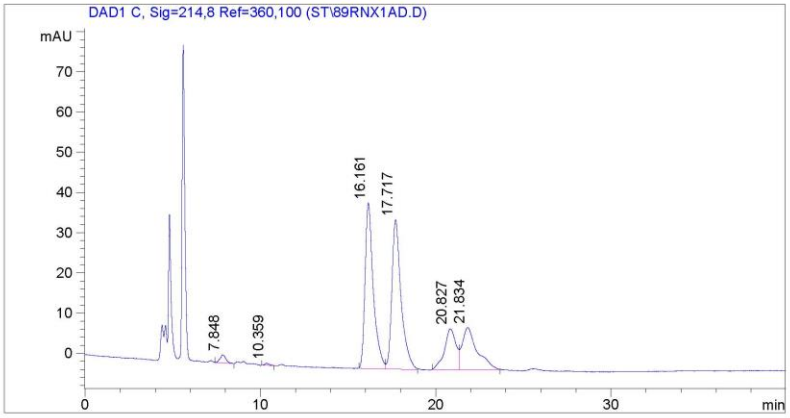


HPLC of **3i**(racemate)

AK Enders - Analytische HPLC

Sample Name:	ST P 89 rac
Data file:	D:\GONZO\ST\89RNX1AD.D
Sample Info:	Laufmittel: n-Heptan/EtOH 97:3; Probe ist in DCM/LM gelöst.
Säule:	DAICELAD.M
Säuleninfo:	Chiralpak AD (250x4,6)mm
Operator:	Analytik Labor AKEN
Injektion Time:	14:11:30
Injektion Date:	16.12.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	22.0	22.3
Flow in ml/min:	0.70	0.70



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	7.85	0.31	2.01	46.69	1.21
2	10.36	0.22	0.58	9.79	0.25
3	16.16	0.48	41.15	1348.24	34.88
4	17.72	0.54	37.13	1360.33	35.19
5	20.83	0.62	10.23	466.77	12.08
6	21.83	0.83	10.51	633.67	16.39
Total				3865.50	100.00

Enantioenriched **3i**

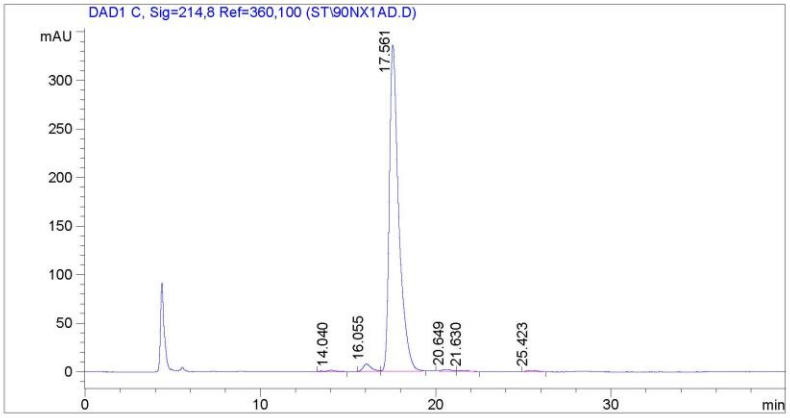
AK Enders - Analytische HPLC

Sample Name: ST P 90
Data file: D:\GONZO\ST\90NX1AD.D
Sample Info: Laufmittel: n-Heptan/EtOH 97:3;
Probe ist in DCM/LM gelöst.

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

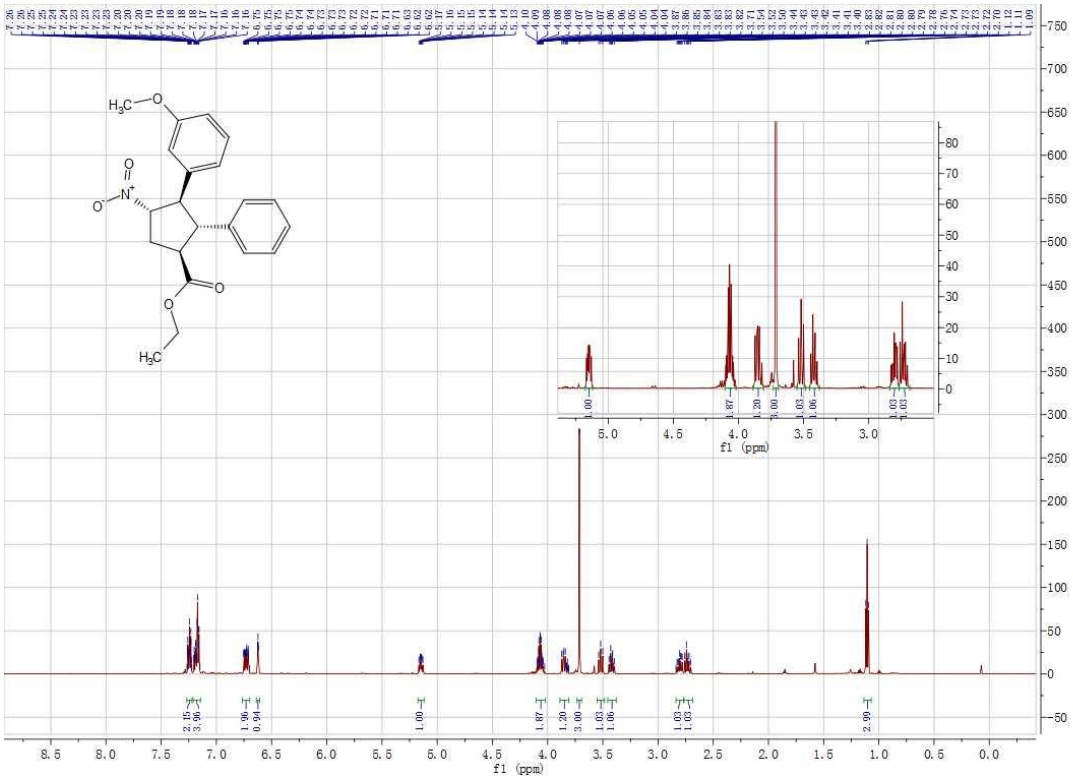
Injektion Time: 14:52:48
Injektion Date: 16.12.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	21.8	22.0
Flow in ml/min:	0.70	0.70

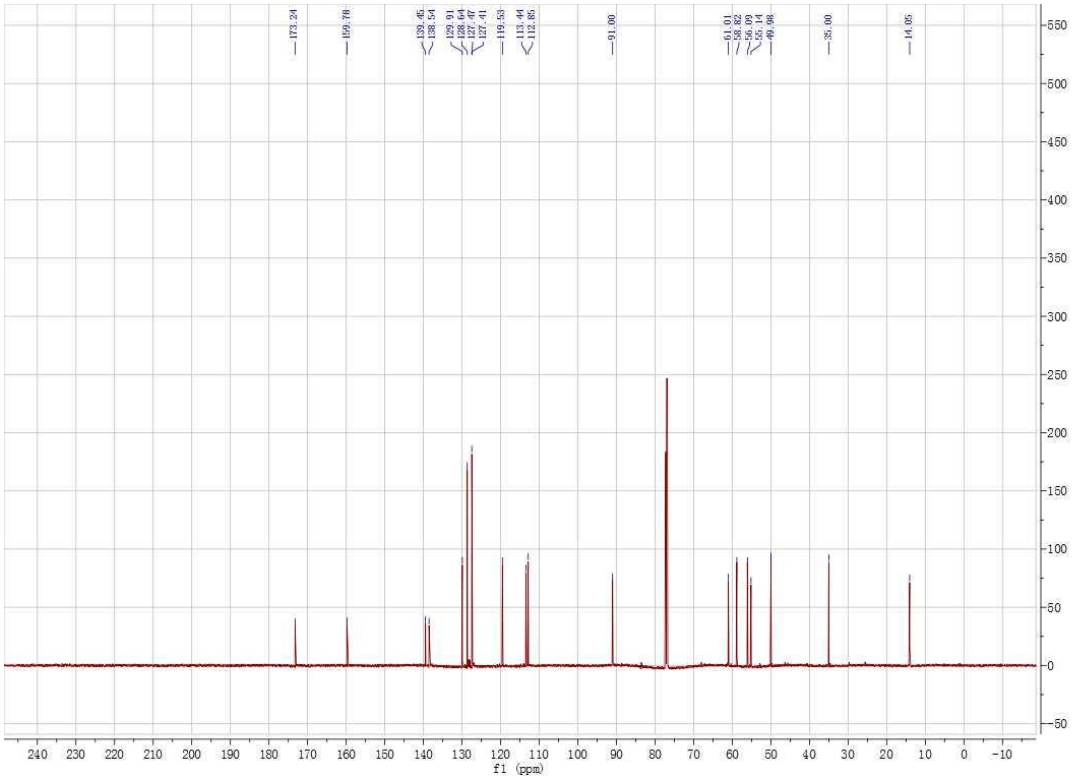


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	14.04	0.50	1.52	59.64	0.46
2	16.05	0.48	7.71	250.10	1.91
3	17.56	0.55	336.04	12615.01	96.27
4	20.65	0.47	1.77	68.59	0.52
5	21.63	0.48	1.10	42.45	0.32
6	25.42	0.52	1.60	68.52	0.52
Total				13104.31	100.00

^{1}H NMR of **3j**



^{13}C NMR of **3j**



HPLC of **3j**(racemate)

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

Sample name: **ST P92 rac**

Data file: C:\SNOOPY\ST\ST P92 RAC IC.D

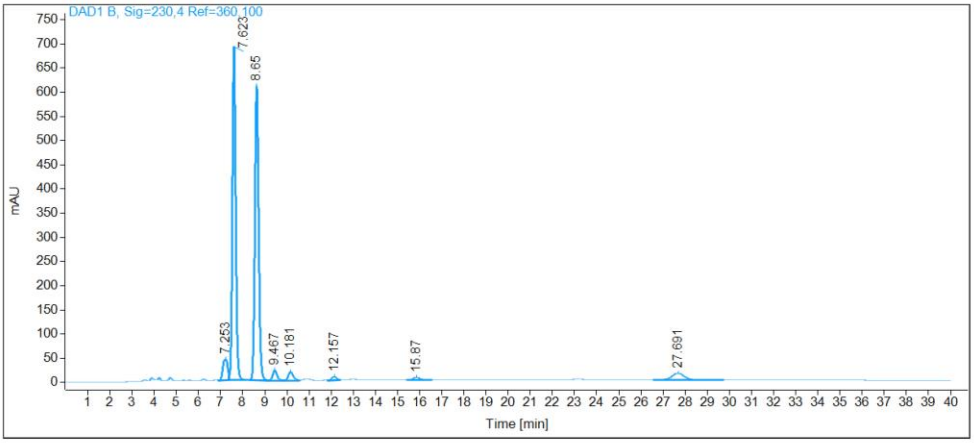
Description: Mobile phase: n-Heptane/EtOH 9:1;
The sample is solved in DCM/MP

Injection date: 12/8/2015 10:25:50 AM

Acq. Analysis method: CHIRALPAKIC1-6LNP.M

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

Pressure at start: 20 bar **Start flow:** 0.500 ml/min **Column oven:** 29.97 °C



Name ST P92 rac

RT [min]	Type	Area%	Area	Height	Width [min]
7.25	BV	4.01	655.66	42.86	0.21
7.62	VB	43.80	7166.16	690.34	0.16
8.65	BV	44.07	7208.96	608.22	0.18
9.47	VV	1.70	278.43	20.53	0.21
10.18	VV	1.68	275.63	18.16	0.23
12.16	VV	0.75	123.33	7.88	0.24
15.87	BV	0.81	132.46	6.07	0.33
27.69	BB	3.17	518.82	13.84	0.58
	Sum	100.00	16359.44		

Agilent 1260 Infinity **Page 1**

Enantioenriched **3j**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

Sample name: **ST P91**

Data file: C:\SNOOPY\ST\ST P91 IC.D

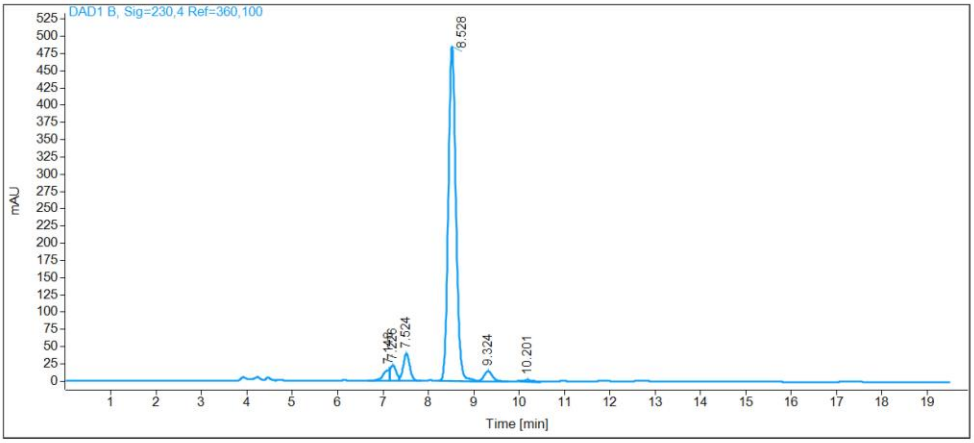
Description: Mobile phase: n-Heptane/EtOH 9:1;
The sample is solved in DCM/MP

Injection date: 12/8/2015 1:08:53 PM

Acq. Analysis method: CHIRALPAKIC1-6LNP.M

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

Pressure at start: 20 bar **Start flow:** 0.500 ml/min **Column oven:** 29.99 °C



Name ST P91

RT [min]	Type	Area%	Area	Height	Width [min]
7.15	MF	2.42	160.21	16.16	0.17
7.23	FM	3.16	209.36	22.57	0.15
7.52	VB	6.06	401.35	39.80	0.15
8.53	BV	85.09	5635.80	484.91	0.18
9.32	VB	2.73	180.54	14.19	0.20
10.20	MM	0.55	36.39	2.08	0.29
	Sum	100.00	6623.64		

Agilent 1260 Infinity **Page 1**