Electronic Supplementary Material (ESI) for ChemComm.

Content

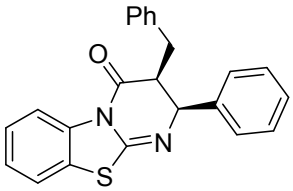
1. General information

- All reactions were carried out under argon. THF and toluene were distilled over Solvona ®. Dichloromethane was distilled over calcium hydride. All other chemicals were used without further purification.
- Triazolium salts **A-G** were prepared according to known literature procedures.[1] Benzothiazolimines **1** were prepared from benzo[*d*]thiazol-2-amine.[2] α-Chloroaldehydes were synthesized form aldehydes.[3] Racemic samples were prepared by using triazolium salt **A** as catalyst, except **3l**, which was prepared by manully mixing **3l** and *ent*-**3l**.
- Chromatographic purification of the products was performed on Merck silica gel 60, particle size 0.040-0.063 mm (230-240 mesh, flash).
- Analytical TLC: SIL G-25 UV254 from MACHEREY&NAGEL. Visualization of the developed TLC plates was performed with ultraviolet irradiation (254 nm).
- Microanalyses were performed with a Vario EL element analyzer.
- 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 Perkin-Elmer FT-IR Spectrum 100 using a Diamant/KRS5 ATR. Evaluation was done using the supplementary software. The absorption bands are given in wave numbers (cm^{-1}).
- ^{1}H- and ^{13}C NMR were recorded at ambient temperature on VNMRS 600 and Inova 400 instruments. The chemical shifts are reported in ppm downfield of tetramethylsilane (TMS) and referenced to residual solvent peaks resonance as internal standard. The order of citation in parentheses is a) multiplicity (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, td = triplet of doublet, m = multiplet), b) coupling constants, c) number of protons, and d) assignment. Coupling constants (J) are reported in Hertz (Hz).
- Analytical HPLC was performed on a Hewlett-Packard 1100 Series instrument using chiral stationary phases (Daicel IC, Daicel IA, Daicel AD, Daicel OJ).
- Optical rotation values were measured on a Perkin-Elmer 241 polarimeter.

2. General procedure

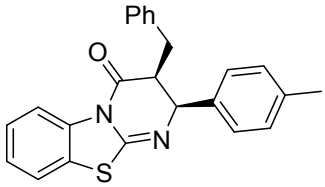
To a dried and argon-filled Schlenk flask was added (*E*)- *N*-arylidenebenzo[d]thiazol-2-amine (**1**) (0.5 mmol, 1.0 equiv.), α-chloroaldehyde **2** (1.0 mmol, 2.0 equiv.), triazolium salt **F** (0.05 mmol, 10 mol%) and DABCO (1.1 mmol, 2.2 equiv.) in toluene (5 ml). The mixture was stirred at room temperature and monitored by TLC until completion of the reaction. The solution was directly purified by flash chromatography on silica gel (pentane/Et_2O 10:1) to afford the products **3a-n**.

3. Characterization Data



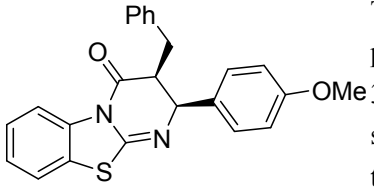
The compound **3a** was prepared according to the general procedure. The product was obtained as a colorless solid (116 mg, 63% yield). The ee (90%) was measured by HPLC using a chiral stationary phase [Daicel IC, *n*-heptane:*i*-PrOH = 9:1, 0.5 mL/min), t_R = 8.85 min (major), 10.43 min (minor)], $[\alpha]_D^{22}$ = +163.8 (c = 1.0, $CHCl_3$). Melting point: 154-155 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.39 (d, *J* = 4.3 Hz, 4H), 7.36 - 7.31 (m, 2H), 7.29 - 7.26 (m, 1H), 7.24 - 7.15 (m, 4H), 7.02 - 6.88 (m, 2H), 5.03 (d, *J* = 5.8 Hz, 1H), 3.31 (ddd, *J* = 7.9, 6.6, 5.8 Hz, 1H), 3.00 (dd, *J* = 14.5, 7.9 Hz, 1H), 2.56 (dd, *J* = 14.5, 6.6 Hz, 1H);
^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.62, 155.83, 138.05, 137.69, 135.62, 128.82 (4C), 128.39 (2C), 127.90, 127.36 (2C), 126.55, 126.50, 125.62, 123.16, 121.75, 116.76, 62.47, 47.38, 31.04;
MS (EI, 70 eV) m/z (%): 370 [M^+] (95), 279 (33), 239 (28), 238 (58), 237 (100);
IR (ATR): 3034, 2928, 1709, 1642, 1453, 1301, 1176, 1014, 913, 865, 745, 697 cm^{-1};
Anal. calcd. for $C_{23}H_{18}N_2OS$ (370) C, 74.57; H, 4.90; N, 7.56 found: C, 74.42; H, 4.91; N, 7.44.



The compound **3b** was prepared according to the general procedure. The product was obtained as a colorless solid (94 mg, 49% yield). 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 = 11.14 min (minor), 11.91 min (major)], $[\alpha]_D^{22}$ = +241.7 (c = 1.0, $CHCl_3$). Melting point: 141-142 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.33 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.25 (ddd, *J* = 6.8, 4.5, 2.1 Hz, 3H), 7.23 - 7.15 (m, 6H), 6.98 (dd, *J* = 6.9, 1.8 Hz, 2H), 4.97 (d, *J* = 5.9 Hz, 1H), 3.30 (td, *J* = 7.3, 6.2 Hz, 1H), 3.02 (dd, *J* = 14.4, 7.6 Hz, 1H), 2.56 (dd, *J* = 14.5, 6.8 Hz, 1H), 2.36 (s, 3H);
^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.71, 155.62, 138.20, 137.61, 135.64, 134.51, 129.49 (2C), 128.83 (2C), 128.38 (2C), 127.25 (2C), 126.51, 126.46, 125.57, 123.19, 121.73, 116.72, 62.29, 47.33, 31.02, 21.13;
MS (EI, 70 eV) m/z (%):384 [M^+] (19), 293 (24), 252 (45), 251 (100), 131 (22), 91 (78);
IR (ATR): 3025, 2930, 1713, 1641, 1506, 1456, 1301, 1174, 1018, 923, 857, 803, 741, 697 cm^{-1};
HRMS (ESI): calcd for $C_{24}H_{20}N_2OS$ $[M+H]^+$: 385.1369; found: 385.1371.



The compound **3c** was prepared according to the general procedure. The product was obtained as a yellow solid (68 mg, 34% yield). The ee (87%) was measured by HPLC using a chiral stationary phase [Daicel IA, *n*-heptane:EtOH = 7:3, 0.7 mL/min), t_R = 14.96 min (minor), 17.15 min (major)], $[\alpha]_D^{22}$ = +167.4 (c = 0.5, $CHCl_3$). Melting point: 149-150 °C.

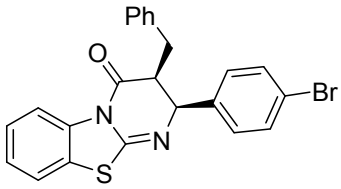
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 (dt, *J* = 8.2, 1.2 Hz, 1H), 7.29 - 7.24 (m, 4H), 7.21 (tt, *J* = 9.9, 2.7 Hz, 4H), 7.03 - 6.96 (m, 2H), 6.95 - 6.87 (m, 2H), 4.95 (d, *J* = 5.9 Hz, 1H), 3.82 (s, 3H), 3.30 (q, *J* = 6.9 Hz, 1H), 3.05 (dd, *J* = 14.5, 7.6 Hz, 1H), 2.55 (dd, *J* = 14.5, 6.9 Hz, 1H);

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.72, 159.25, 155.57, 138.21, 135.63, 131.35, 128.82 (2C), 128.53(2C), 128.41 (2C), 126.52, 126.48, 125.58, 123.17, 121.74, 116.71, 114.19 (2C), 61.97, 55.28, 47.35, 31.01;

MS (EI, 70 eV) m/z (%):400 [M^+] (22), 308 (35), 268 (88), 267 (96), 135 (100), 91 (43);

IR (ATR): 3064, 3024, 2928, 2842, 1715, 1638, 1509, 1455, 1293, 1246, 1173, 1028, 911, 826, 743, 697 cm^{-1};

HRMS (ESI): calcd for $C_{24}H_{20}N_2O_2S$ [M+Na] $^+$: 423.1138; found: 423.1131.



The compound **3d** was prepared according to the general procedure. The product was obtained as a colorless solid (125 mg, 56% yield). The ee (91%) was measured by HPLC using a chiral stationary phase [Daicel IA, *n*-heptane:EtOH = 7:3, 0.7 mL/min), t_R = 12.98 min (minor), 15.30 min (major)], $[\alpha]_D^{22}$ = +164.5 (c = 1.0, $CHCl_3$). Melting point: 167-168 °C.

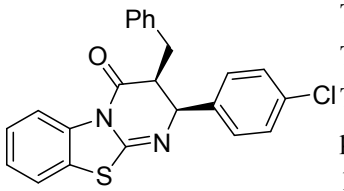
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 - 8.10 (m, 1H), 7.59 - 7.07 (m, 10H), 6.92 (dd, *J* = 7.4, 2.0 Hz, 2H), 4.98 (d, *J* = 5.6 Hz, 1H), 3.25 (ddd, *J* = 8.0, 6.5, 5.6 Hz, 1H), 2.93 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.52 (dd, *J* = 14.4, 6.6 Hz, 1H);

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.32, 156.21, 137.62, 136.92, 135.51, 131.88 (2C), 129.04 (2C), 128.76 (2C), 128.43 (2C), 126.65, 126.57, 125.74, 123.04, 121.78, 121.75, 116.80, 61.75 , 47.24, 31.03;

MS (EI, 70 eV) m/z (%):450 [M+2] (50), 448 [M^+] (44), 359 (35), 357 (34), 318 (76), 317 (100), 316 (67), 315 (78), 135 (24), 91 (19);

IR (ATR): 3027, 2926, 1714, 1638, 1582, 1485, 1458, 1299, 1180, 1004, 914, 858, 801, 746, 694 cm^{-1};

HRMS (ESI): calcd for $C_{23}H_{17}BrN_2OS$ [M+Na]$^+$: 471.0137; found: 471.0138.



The compound **3e** was prepared according to the general procedure. The product was obtained as a colorless solid (123 mg, 61% yield). The ee (89%) was measured by HPLC using a chiral stationary phase [Daicel AD, *n*-heptane:EtOH = 9:1, 1.0 mL/min), t_R = 12.07min (minor), 14.44 min (major)], $[\alpha]_D^{22}$ = +166.0 (c = 1.0, $CHCl_3$). Melting point: 162-163 °C.

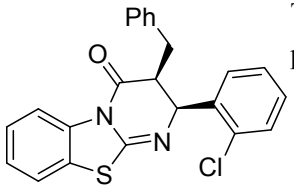
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.24 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.49 - 7.12 (m, 10H), 7.04 - 6.83 (m, 2H), 5.01 (d, *J* = 5.6 Hz, 1H), 3.35 - 3.20 (m, 1H), 2.95 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.53 (dd, *J* = 14.5, 6.6 Hz, 1H);

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.35, 156.24, 137.66, 136.38, 135.53, 133.65, 128.95 (2C), 128.77 (2C), 128.72 (2C), 128.44 (2C), 126.66, 126.59, 123.06, 125.75, 121.79, 116.81, 61.71, 47.30, 31.03;

MS (EI, 70 eV) m/z (%): 406 [M+2] (33), 404 [M^+] (83), 313 (35), 274 (30), 272 (89), 270 (100), 135 (33), 91 (90);

IR (ATR): 3062, 2933, 1714, 1638, 1463, 1301, 1177, 1093, 1009, 923, 852, 808, 740, 696 cm^{-1};

Anal. calcd. for $C_{23}H_{17}ClN_2OS$ (404) C, 68.22; H, 4.23; N, 6.92 found: C, 68.42; H, 4.15; N, 6.56.



The compound **3f** was prepared according to the general procedure. The product was obtained as a colorless solid (121 mg, 60% yield). The ee

(97%) was measured by HPLC using a chiral stationary phase [Daicel OJ, *n*-heptane:EtOH = 7:3, 0.7 mL/min), t_R = 13.20 min (major), 17.14 min (minor)], $[\alpha]_D^{22}$ = +253.8 (c = 1.0, $CHCl_3$). Melting point: 170-171 °C.

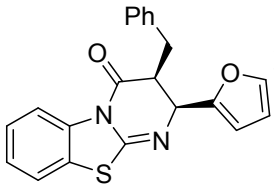
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 - 7.66 (m, 2H), 7.42 - 7.35 (m, 2H), 7.33 - 7.24 (m, 4H), 7.23 - 7.16 (m, 3H), 7.07 - 6.93 (m, 2H), 5.93 (d, *J* = 6.1 Hz, 1H), 4.18 (ddd, *J* = 9.0, 6.8, 6.1 Hz, 1H), 2.75 (dd, *J* = 14.6, 9.0 Hz, 1H), 2.56 (dd, *J* = 14.6, 6.8 Hz, 1H);

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.70, 149.30, 137.18, 133.28, 132.24, 131.89, 129.79, 129.51, 128.69 (2C), 128.38 (2C), 127.75, 126.97, 126.58, 126.32, 124.32, 122.68, 122.00, 121.36, 58.69, 56.38, 31.66;

MS (EI, 70 eV) m/z (%):406 [M+2] (7), 404 [M^+] (19), 237 (100), 91 (22);

IR (ATR): 3061, 2934, 1765, 1597, 1520, 1441, 1355, 1274, 1033, 899, 749, 668 cm^{-1};

HRMS (ESI): calcd for $C_{23}H_{17}ClN_2OS$ [M+Na]$^+$: 427.0642; found: 427.0637.



The compound **3g** was prepared according to the general procedure. The product was obtained as a colorless solid (124 mg, 69% yield). The ee (93%) was measured by HPLC using a chiral stationary phase [Daicel AD, *n*-heptane:EtOH = 7:3, 0.7 mL/min), t_R = 10.76 min (minor), 13.45 min (major)], $[\alpha]_D^{22}$ = +336.9 (c = 1.0, $CHCl_3$). Melting point: 52-53 °C.

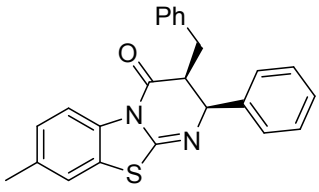
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 - 8.27 (m, 1H), 7.34 (s, 1H), 7.32 - 7.26 (m, 3H), 7.25 - 7.17 (m, 3H), 7.12 (d, *J* = 7.0 Hz, 2H), 6.37 - 6.24 (m, 2H), 4.82 (d, *J* = 6.5 Hz, 1H), 3.41 (dd, *J* = 14.3, 5.1 Hz, 1H), 3.32 (ddd, *J* = 9.1, 6.5, 5.1 Hz, 1H), 2.42 (dd, *J* = 14.3, 9.0 Hz, 1H);

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.06, 157.52, 150.43, 142.81, 138.30, 135.79, 128.85 (2C), 128.54 (2C), 126.63, 126.50, 125.47, 123.01, 121.67, 116.72, 110.22, 109.12, 55.95, 45.24, 30.99;

MS (EI, 70 eV) m/z (%):362 [M+2] (25), 361 [M+1] (72), 360 [M^+] (100), 269 (50), 228 (71), 200 (37), 187 (30), 91 (26);

IR (ATR): 3028, 2927, 1719, 1633, 1462, 1301, 1172, 817, 740, 703 cm^{-1};

HRMS (ESI): calcd for $C_{21}H_{17}N_2O_2S$ [M+H]$^+$: 361.1005; found: 361.1001.



The compound **3h** was prepared according to the general procedure. The product was obtained as a colorless solid (123 mg, 64% yield). The ee (93%) was measured by HPLC using a chiral stationary phase [Daicel IC, *n*-heptane:*i*-PrOH = 9:1, 0.5 mL/min), t_R = 10.54 min (major), 12.31 min (minor)], $[\alpha]_D^{22}$ = +150.9 (c = 1.0, $CHCl_3$). Melting point: 153-154 °C.

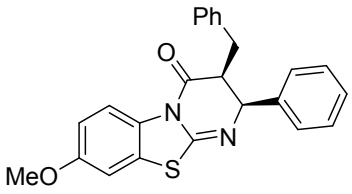
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.41 – 7.27 (m, 5H), 7.22 – 7.10 (m, 4H), 7.09 – 7.00 (m, 1H), 7.00 – 6.87 (m, 2H), 5.00 (d, *J* = 5.8 Hz, 1H), 3.28 (dt, *J* = 7.9, 6.3 Hz, 1H), 2.97 (dd, *J* = 14.4, 7.9 Hz, 1H), 2.54 (dd, *J* = 14.4, 6.6 Hz, 1H), 2.35 (s, 3H);

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.44, 156.08, 138.10, 137.77, 135.65, 133.36, 128.81 (2C), 128.78 (2C), 128.36 (2C), 127.84, 127.35 (2C), 127.12, 126.51, 123.02, 122.09, 116.46, 62.47, 47.32, 31.03, 21.12;

MS (EI, 70 eV) m/z (%):385 [M+1] (37), 384 [M^+] (87), 293 (41), 253 (30), 252 (84), 251 (100), 91 (25);

IR (ATR): 3029, 2923, 1718, 1633, 1476, 1297, 1170, 910, 873, 819, 743, 699 cm^{-1};

HRMS (ESI): calcd for $C_{24}H_{20}N_2OS$ [M+H]$^+$: 385.1369; found: 385.1372.



The compound **3i** was prepared according to the general procedure. The product was obtained as a colorless solid (111 mg, 56% yield). The ee (92%) was measured by HPLC using a chiral stationary phase [Daicel AD, *n*-heptane:EtOH = 7:3, 0.7 mL/min), t_R = 13.39 min (minor), 16.40 min (major)], $[\alpha]_D^{22}$ = +131.0 (c = 1.0, $CHCl_3$).

Melting point: 144-145 °C.

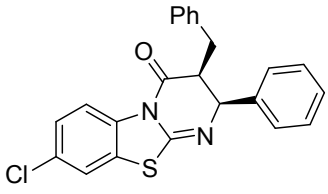
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 9.0 Hz, 1H), 7.41 - 7.28 (m, 5H), 7.22 - 7.14 (m, 3H), 6.97 - 6.93 (m, 2H), 6.89 (d, *J* = 2.6 Hz, 1H), 6.78 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.02 (d, *J* = 5.8 Hz, 1H), 3.82 (d, *J* = 0.8 Hz, 3H), 3.28 (ddd, *J* = 7.9, 6.6, 5.7 Hz, 1H), 2.97 (dd, *J* = 14.5, 7.9 Hz, 1H), 2.55 (dd, *J* = 14.4, 6.6 Hz, 1H);

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.25, 157.47, 156.04, 138.10, 137.80, 128.83 (2C), 128.79 (2C), 128.36 (2C), 127.85, 127.36 (2C), 126.52, 124.44, 117.54, 111.70, 107.57, 104.56, 62.55, 55.71, 47.23, 31.03;

MS (EI, 70 eV) m/z (%): 401 [M+1] (32), 400 [M^+] (93), 268 (100), 267 (89), 253 (22), 91 (18);

IR (ATR): 3061, 3027, 2964, 2841, 1713, 1641, 1595, 1479, 1328, 1255, 1175, 1027, 916, 881, 827, 741, 696 cm^{-1};

Anal. calcd. for $C_{24}H_{20}N_2O_2S$ (400) C, 71.98; H, 5.03; N, 6.99 found: C, 71.64; H, 5.17; N, 6.59.



The compound **3j** was prepared according to the general procedure. The product was obtained as a colorless solid (157 mg, 78% yield). The ee (91%) was measured by HPLC using a chiral stationary phase [Daicel IC, *n*-heptane:EtOH = 7:3, 0.5 mL/min), t_R = 18.59 min (minor), 20.67 min (major)], $[\alpha]_D^{22}$ = +109.1 (c = 1.0, $CHCl_3$).

Melting point: 63-64 °C.

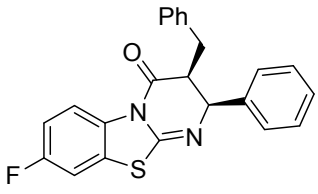
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.8 Hz, 1H), 7.42 - 7.12 (m, 10H), 7.01 - 6.87 (m, 2H), 5.02 (d, *J* = 5.8 Hz, 1H), 3.29 (ddd, *J* = 7.9, 6.5, 5.7 Hz, 1H), 2.95 (dd, *J* = 14.4, 7.9 Hz, 1H), 2.55 (dd, *J* = 14.4, 6.6 Hz, 1H);

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.44, 155.12, 137.82, 137.47, 134.14, 131.00, 128.86 (2C), 128.80 (2C), 128.41 (2C), 127.98, 127.28 (2C), 126.63, 126.59, 124.95, 121.64, 117.46, 62.53, 47.29, 31.03;

MS (EI, 70 eV) m/z (%): 406 [M+2] (10), 404 [M^+] (27), 274 (32), 273 (57), 272 (81), 271 (100), 91 (90);

IR (ATR): 3063, 3028, 2927, 1720, 1640, 1577, 1459, 1291, 1176, 1144, 1086, 908, 865, 816, 736, 697 cm^{-1};

HRMS (ESI): calcd for $C_{23}H_{17}ClN_2OS$ $[M+Na]^+$: 427.0642; found: 427.0640.

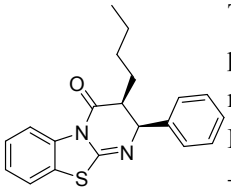


The compound **3k** was prepared according to the general procedure. The product was obtained as a colorless solid (138 mg, 71% yield). The ee (89%) was measured by HPLC using a chiral stationary phase [Daicel IA, *n*-heptane:EtOH = 7:3, 0.5 mL/min), t_R = 16.22 min (minor), 17.76 min (major)], $[\alpha]_D^{22}$ = +126.4 (c = 1.0, $CHCl_3$).

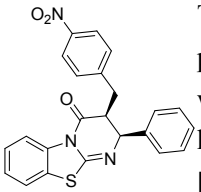
Melting point: 55-56 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (dd, *J* = 9.1, 4.8 Hz, 1H), 7.40 - 7.31 (m, 5H), 7.22 - 7.13

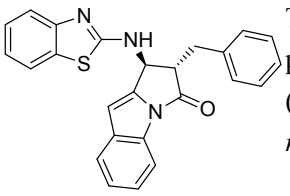
(m, 3H), 7.06 (dd, *J* = 7.7, 2.6 Hz, 1H), 6.94 (dd, *J* = 7.2, 1.6 Hz, 3H), 5.02 (d, *J* = 5.8 Hz, 1H), 3.29 (ddd, *J* = 7.8, 6.6, 5.8 Hz, 1H), 2.95 (dd, *J* = 14.4, 7.8 Hz, 1H), 2.55 (dd, *J* = 14.3, 6.6 Hz, 1H);
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.40, 160.08 (d, *J* = 246.4 Hz), 155.46, 137.71 (d, *J* = 35.8 Hz), 131.88, 131.40, 128.85 (2C), 128.81 (2C), 128.40 (2C), 127.95, 127.31 (2C), 126.60, 124.90 (d, *J* = 9.9 Hz), 117.74 (d, *J* = 8.3 Hz), 113.24 (d, *J* = 22.9 Hz), 109.31 (d, *J* = 27.3 Hz), 62.55, 47.22, 31.03;
MS (EI, 70 eV) m/z (%):388 [M^+] (66), 257 (26), 256 (86), 255 (100);
IR (ATR): 3062, 3030, 2928, 2856, 1719, 1640, 1592, 1471, 1221, 1164, 899, 852, 749, 698 cm^{-1};
HRMS (ESI): calcd for $C_{23}H_{17}FN_2OS$ [M+Na]$^+$: 411.0938; found: 427.0934.



The compound **3l** was prepared according to the general procedure. The product was obtained as a yellow oil (86 mg, 51% yield). The ee (87%) was measured by HPLC using a chiral stationary phase [Daicel IC, *n*-heptane:*i*-PrOH = 9:1, 0.7 mL/min), t_R = 4.90 min (minor), 5.41 min (major)], $[\alpha]_D^{22}$ = +47.9 (c = 1.0, $CHCl_3$).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.42 - 7.31 (m, 5H), 7.31 - 7.18 (m, 3H), 5.05 (d, *J* = 5.2 Hz, 1H), 2.93 - 2.78 (m, 1H), 1.57 - 1.46 (m, 1H), 1.30 - 1.16 (m, 4H), 0.92 - 0.84 (m, 1H), 0.75 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.66, 155.64, 138.30, 135.78, 128.57 (2C), 127.51, 127.12 (2C), 126.45, 125.58, 123.32, 121.76, 116.90, 62.57, 45.77, 29.28, 24.15, 22.35, 13.71;
MS (EI, 70 eV) m/z (%):336 [M^+] (24), 334 (43), 292 (29), 291 (100), 254 (25), 237 (37), 105 (63), 77 (30);
IR (ATR): 3891, 3775, 3383, 3118, 2624, 2441, 2287, 2184, 2099, 1949, 1587, 1464, 1269, 1178, 1108, 933, 802, 720;
HRMS (ESI): calcd for $C_{20}H_{20}N_2OS$ [M+H]$^+$: 337.1369; found: 337.1369.



The compound **3m** was prepared according to the general procedure. The product was obtained as a colorless solid (143 mg, 69% yield). The ee (92%) was measured by HPLC using a chiral stationary phase [Daicel IC, *n*-heptane:EtOH = 7:3, 0.7 mL/min), t_R = 27.73 min (major), 39.53 min (minor)], $[\alpha]_D^{22}$ = +110.4.1 (c = 0.5, $CHCl_3$). Melting point: 186-187 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.30 (m, 6H), 7.25 (ddd, *J* = 9.0, 7.5, 1.6 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 5.05 (d, *J* = 5.7 Hz, 1H), 3.30 (dt, *J* = 8.4, 5.8 Hz, 1H), 2.96 (dd, *J* = 14.4, 8.3 Hz, 1H), 2.67 (dd, *J* = 14.4, 5.9 Hz, 1H);
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.95, 155.88, 146.71, 146.09, 137.39, 135.34, 129.74 (2C), 128.97 (2C), 128.13, 127.19 (2C), 126.65, 125.95, 123.57 (2C), 123.09, 121.88, 116.82, 62.44, 47.18, 31.27;
MS (EI, 70 eV) m/z (%):415 [M^+] (36), 238 (49), 237 (100);
IR (ATR): 3064, 2926, 2849, 1707, 1650, 1448, 1338, 1276, 1176, 1105, 854, 748, 702 cm^{-1};
HRMS (ESI): calcd for $C_{23}H_{17}N_3O_3S$ [M+H]$^+$: 416.1063; found: 416.1063.



The compound **3n** was prepared according to the general procedure. The product was obtained as a colorless solid (91 mg, 45% yield). The ee (93%) was measured by HPLC using a chiral stationary phase [Daicel IA, *n*-heptane:EtOH = 7:3, 0.7 mL/min), t_R = 10.10 min (minor), 12.19 min

(major)], $[\alpha]_D^{22}$ = -76.2 (c = 0.5, $CHCl_3$). Melting point: 78-79 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (dq, *J* = 8.0, 0.9 Hz, 1H), 7.57 (ddd, *J* = 8.4, 7.2, 1.1 Hz, 2H), 7.47 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.39 - 7.26 (m, 5H), 7.24 - 7.11 (m, 4H), 6.45 (d, *J* = 1.0 Hz, 1H), 5.51 (s, 1H), 5.43 (dd, *J* = 4.2, 1.4 Hz, 1H), 3.51 - 3.44 (m, 2H), 3.37 (dd, *J* = 15.4, 8.2 Hz, 1H);

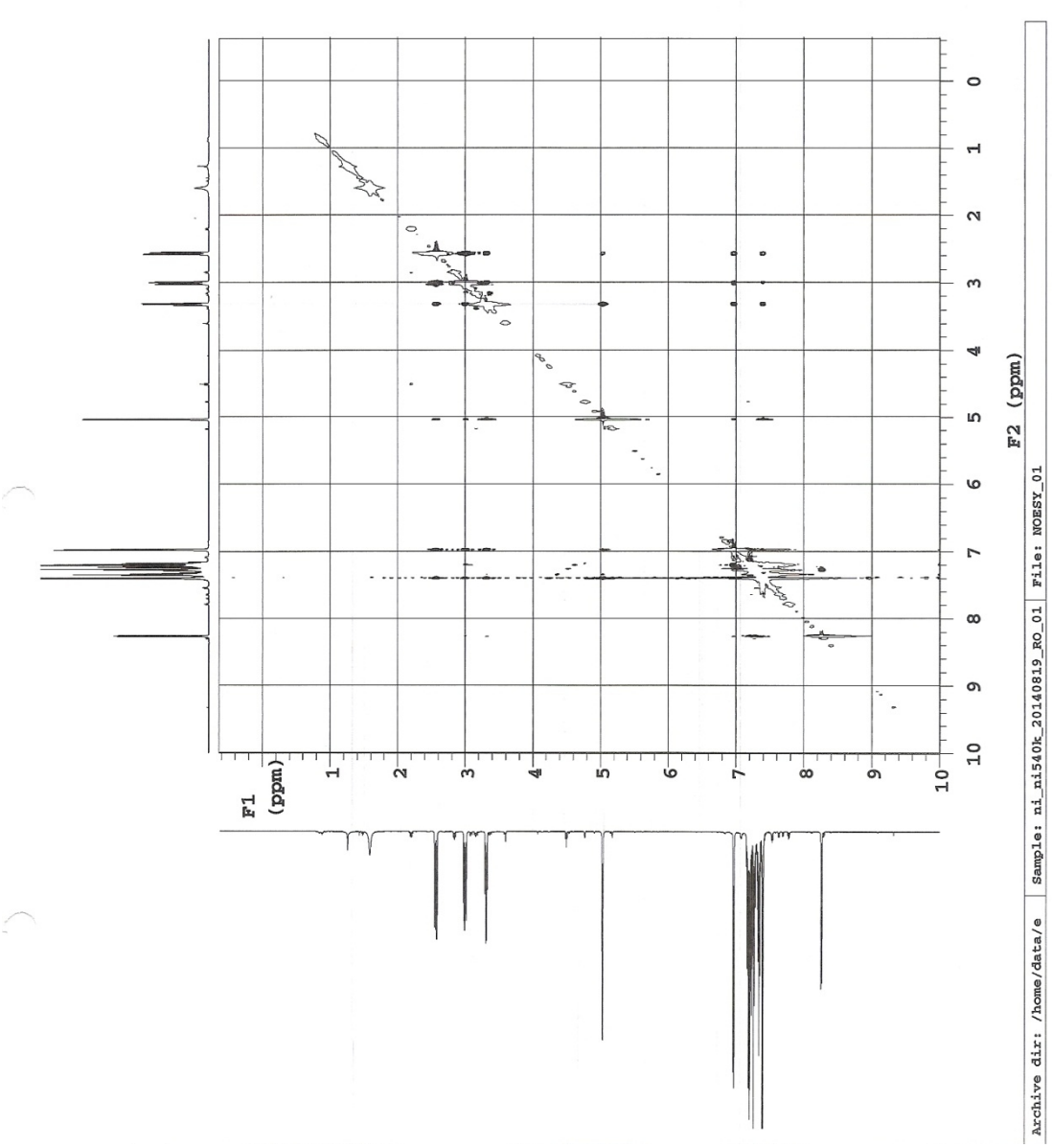
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.56, 164.85, 151.99, 141.23, 137.06, 134.60, 130.96, 130.37, 129.49 (2C), 128.70 (2C), 126.98, 126.08, 124.44, 124.39, 122.38, 121.32, 120.87, 119.66, 114.09, 102.52, 56.74, 52.09, 35.20;

MS (ESI) m/z (%):410.1314 [M+H], 432.1132 [M+Na];

IR (ATR): 2932, 2564, 2176, 2026, 1736, 1616, 1537, 1447, 1365, 1215, 1133, 1018, 935, 747, 699;

HRMS (ESI): calcd for $C_{25}H_{19}N_3OS$ $[M+Na]^+$: 432.1141; found: 432.1130.

4. The NOESY spectrum of 3a



5. References

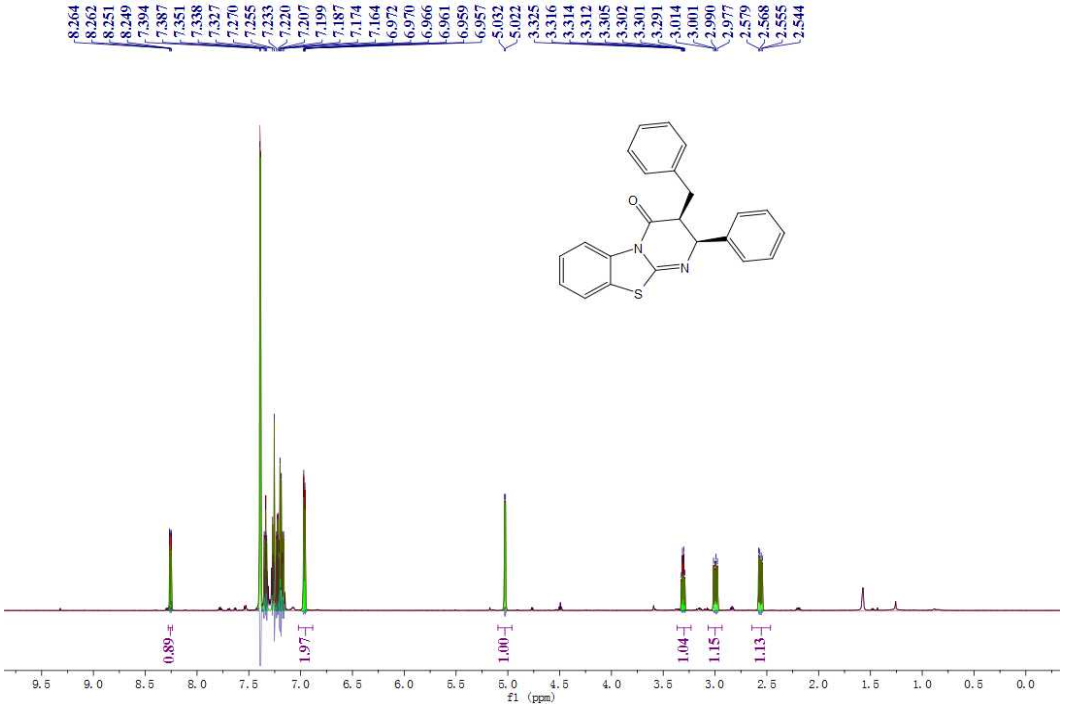
[1] a) N. E. Wurz, C. G. Daniliuc and F. Glorius, *Chem. Eur. J.*, 2012, **18**, 16297; b) H. U. Vora, S. P. Lathrop, N. T. Reynolds, M. S. Kerr, J. V. R. de Alaniz and T. Rovis, *Org. Synth.*, 2010, **87**, 350; c) J. R. Struble and J. W. Bode, *Org. Synth.*, 2010, **87**, 362; d) K. B. Ling and A.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

[2] a) T.-S. Jin, M.-J. Yu, L.-B. Liu, Y. Zhao and T.-S. Li, *Synth. Commun.*, 2006, **36**, 2339.

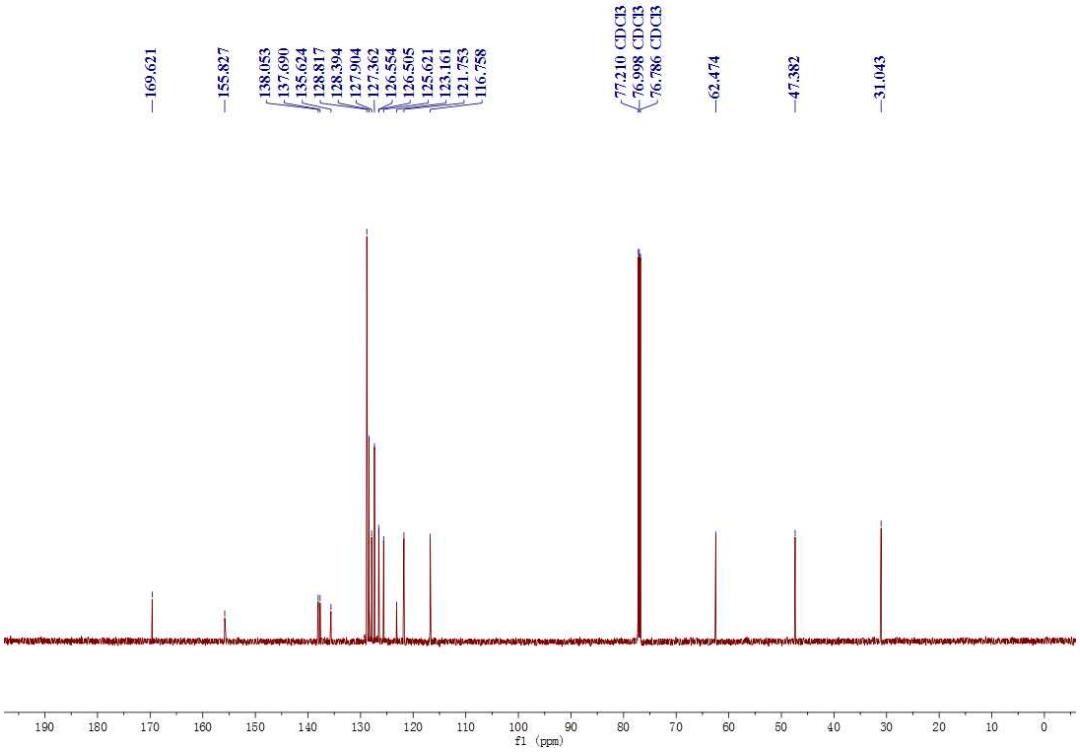
[3] a) T. Borg, J. Danielsson and P. Somfai, *Chem. Commun.*, 2010, **46**, 1281; b) N. Halland, A. Braunton, S. Bachmann, M. Marigo and K. A. Jorgensen, *J. Am. Chem. Soc.*, 2004, **126**, 4790.

6. Copies of NMR spectra and HPLC measurements of the products *cis*-3 (plus minor trans-isomer)

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



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



HPLC analysis: rac-**3a**

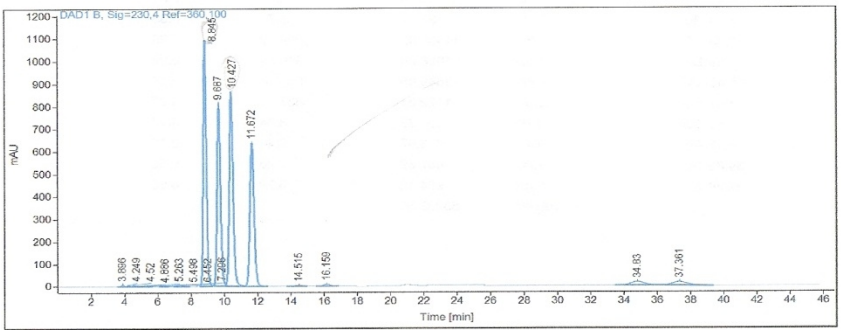
Sample name: **NI 61a rac**

Data file: C:\SNOOPY\NI\NI 61A RAC 1IC.D
Description: Laufmittel: n-Heptan/IP 9:1 Die Probe ist DCM/LM gelöst.

Injection date: 5/26/2014 8:55:07 AM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

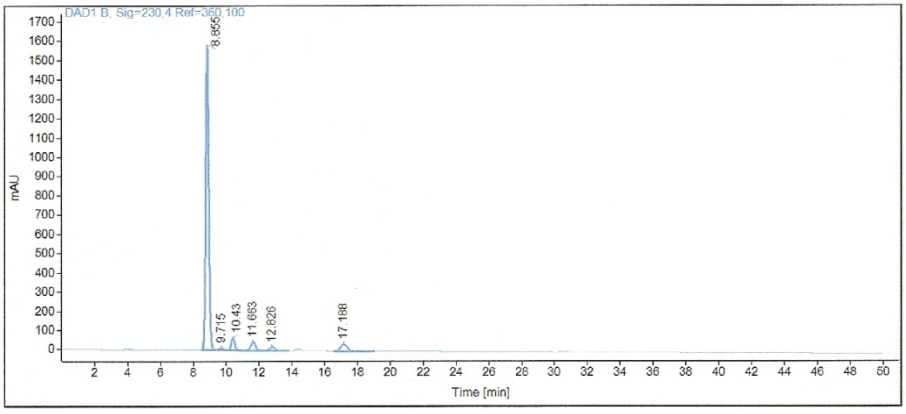
Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 21 bar **Start flow:** 0.500 ml/min **Column oven:** 29.99 °C



RT [min]	Type	Area%	Area	Height	Width [min]
3.90	BV	0.13	71.55	7.81	0.15
4.25	VB	0.10	53.30	7.22	0.11
4.52	BV	0.09	48.72	6.34	0.11
4.89	VB	0.04	18.76	1.54	0.16
5.26	BV	0.12	62.86	4.36	0.19
5.50	VB	0.04	18.99	2.52	0.11
6.45	BB	0.08	39.98	2.09	0.29
7.30	BB	0.26	137.81	6.73	0.33
8.85	VB	26.31	14009.02	1094.42	0.20
9.69	BV	21.86	11638.69	810.51	0.22
10.43	VV	25.64	13649.05	863.14	0.24
11.67	VB	20.99	11172.31	637.20	0.27
14.51	BB	0.19	101.32	3.64	0.42
16.16	BB	0.46	243.07	9.44	0.40
34.83	BB	1.86	987.69	17.28	0.88
37.36	BB	1.85	984.42	16.29	0.95
	Sum	100.00	53237.56		

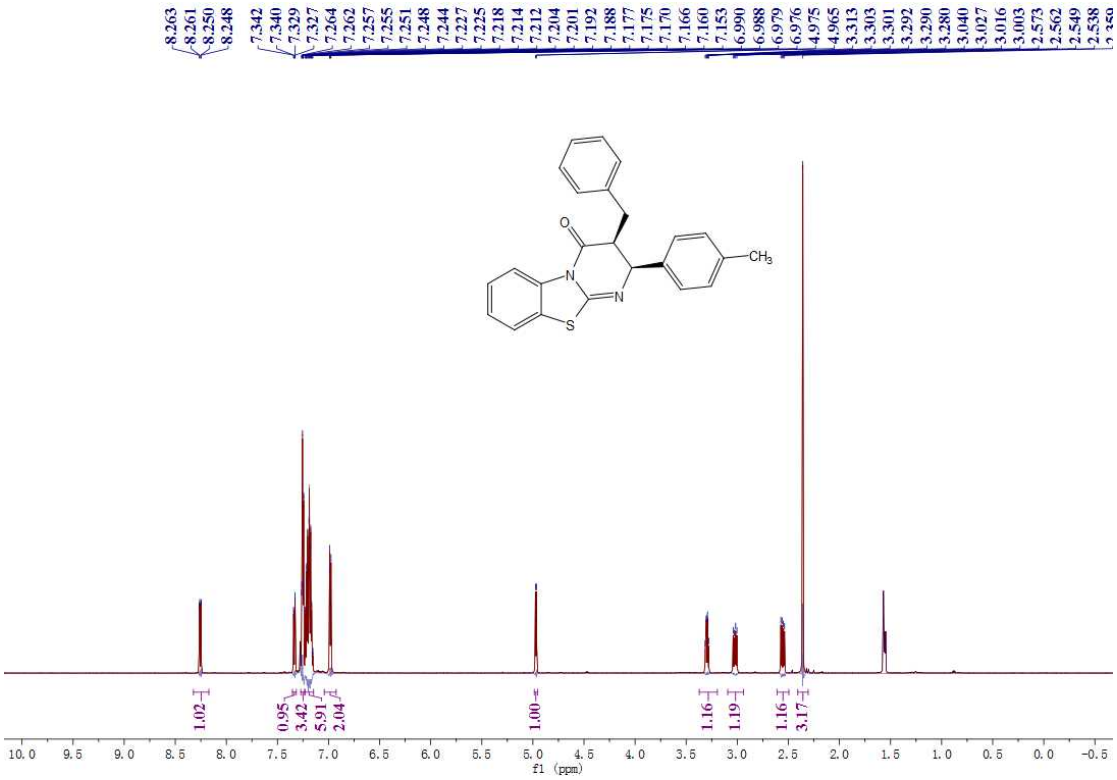
Enantioenriched **3a**



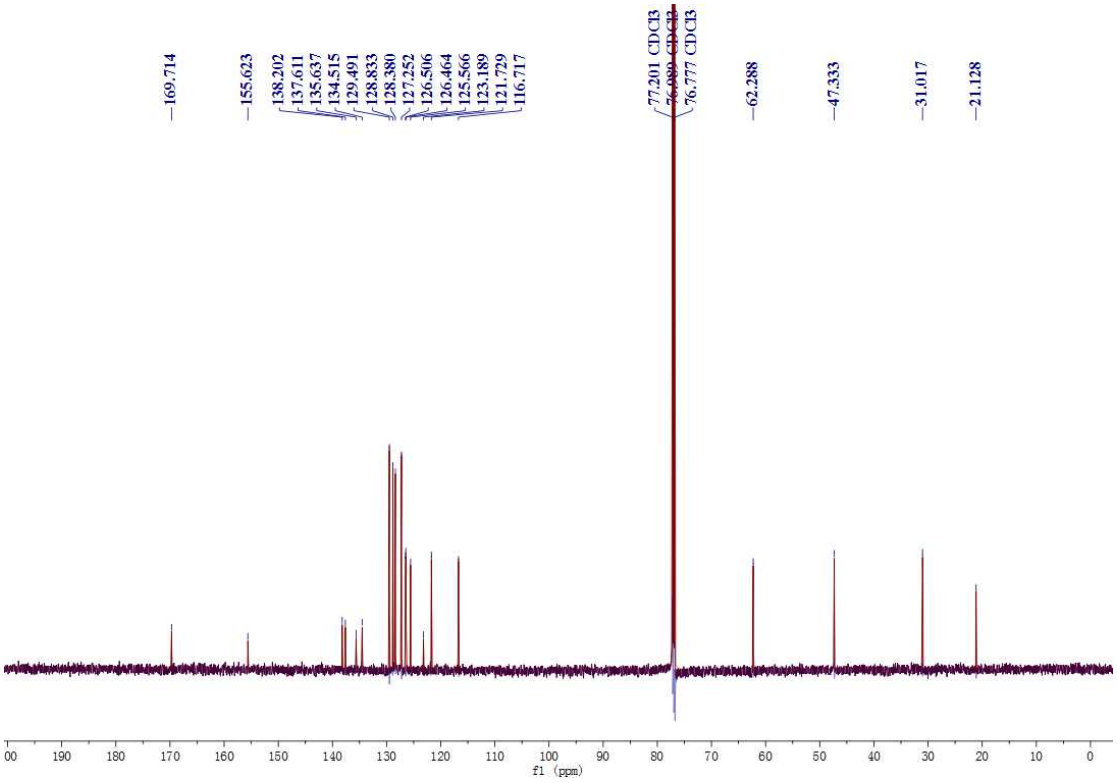
Name Ni 61 ac

RT [min]	Type	Area%	Area	Height	Width [min]
8.86	BV	85.42	20360.34	1585.23	0.20
9.71	VB	0.79	189.42	12.08	0.24
10.43	BB	4.33	1031.69	65.60	0.24
11.66	BB	3.63	865.41	45.11	0.29
12.83	BB	1.71	407.85	20.15	0.32
17.19	BB	4.11	980.72	34.84	0.44
	Sum	100.00	23835.43		

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

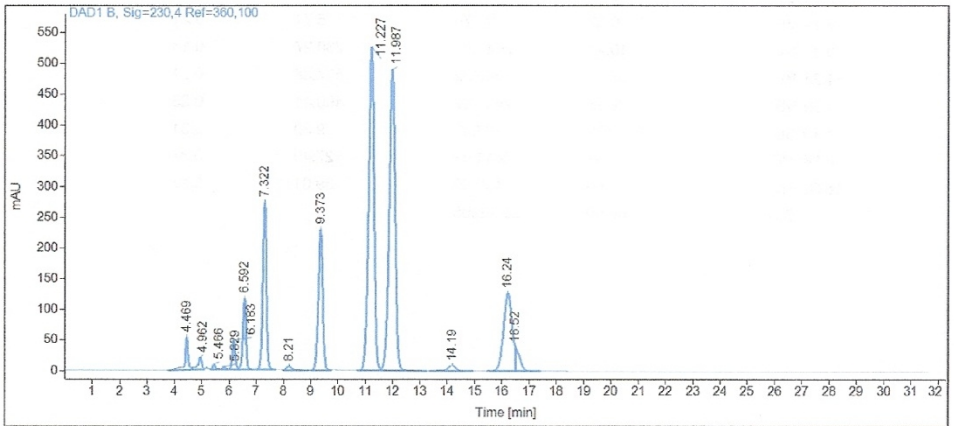


^{13}C NMR of **3b**



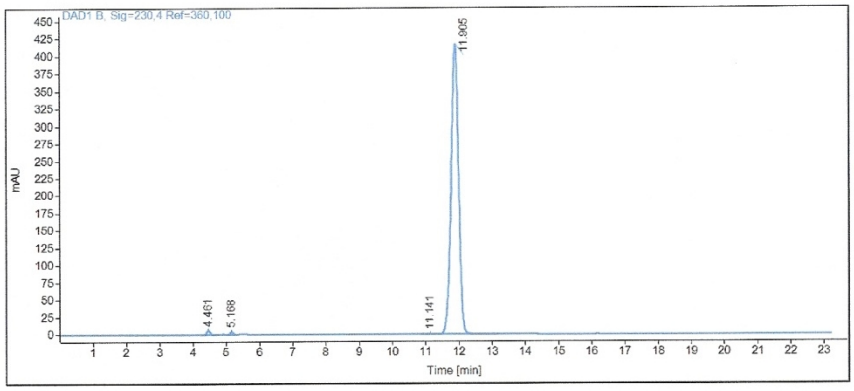
HPLC analysis: rac-**3b**

Sample name:	**Ni 74 a**
Data file:	C:\SNOOPY\NI\74AR1IA.D
Description:	Laufmittel: n-Heptan/EtOH 7:3; Probe ist in LM/DCM gelöst.
Injection date:	8/22/2014 1:05:09 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:	30 °C



RT [min]	Type	Area%	Area	Height	Width [min]
4.47	BV	1.69	429.19	54.69	0.11
4.96	VV	0.78	199.02	20.47	0.14
5.47	BB	0.20	51.75	8.00	0.10
5.83	BV	0.12	29.65	4.45	0.11
6.18	VV	1.44	364.98	48.25	0.12
6.59	VB	3.59	911.82	117.22	0.12
7.32	BV	9.70	2463.09	273.82	0.14
8.21	VB	0.32	81.70	5.74	0.21
9.37	BV	10.41	2643.95	230.27	0.18
11.23	BV	28.93	7349.52	527.38	0.21
11.99	VB	29.37	7459.97	490.41	0.23
14.19	BB	0.78	197.50	9.30	0.31
16.24	MF	11.07	2811.93	127.40	0.37
16.52	FM	1.60	406.90	39.01	0.17
Sum		100.00	25400.95		

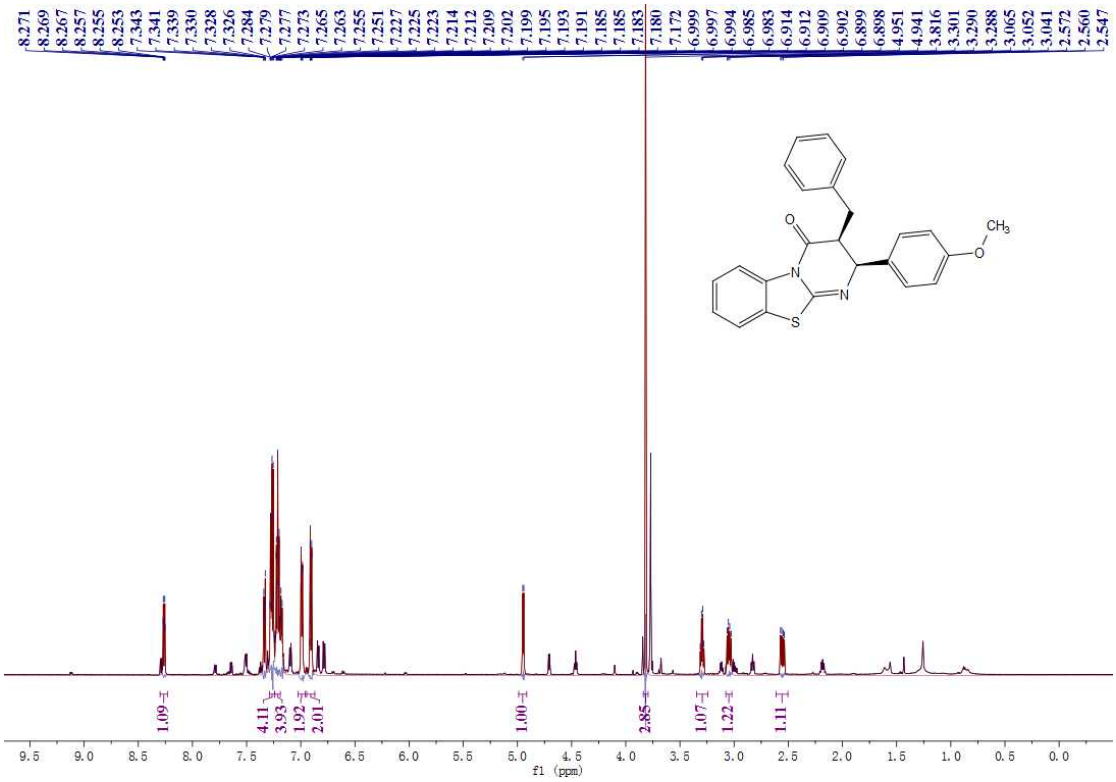
Enantioenriched **3b**



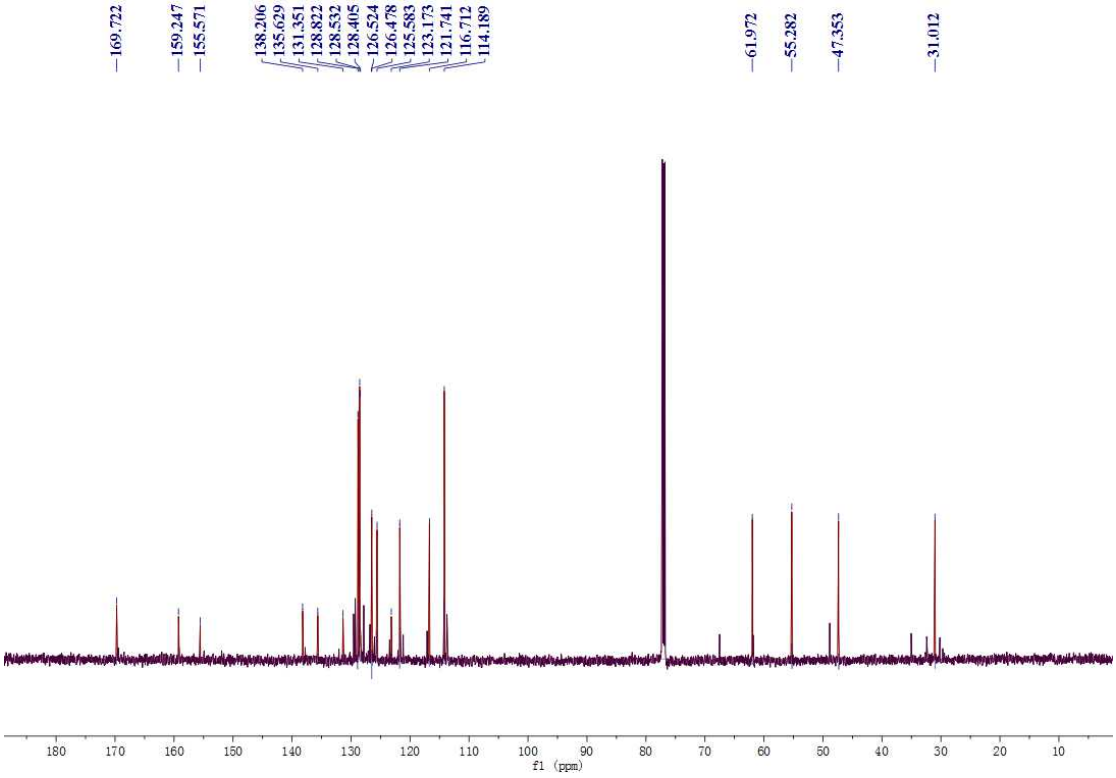
Name Ni 74 b

RT [min]	Type	Area%	Area	Height	Width [min]
4.46	VV	0.78	51.45	6.39	0.12
5.17	VV	0.48	31.42	4.21	0.11
11.14	BB	0.07	4.87	0.38	0.20
11.91	BB	98.67	6504.04	416.61	0.24
Sum		100.00	6591.78		

^{1}H NMR of **3c** (diastereomeric mixture)



^{13}C NMR of **3c** (diastereomeric mixture)



HPLC analysis: rac-**3c**

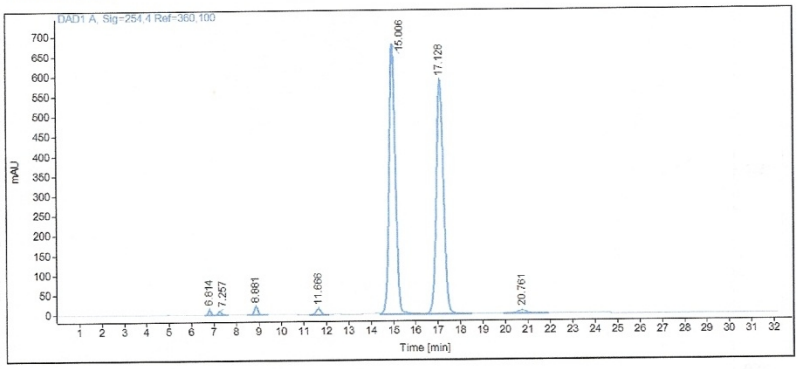
Sample name: **Ni 75 a rac**

Data file: C:\SNOOPY\NI\NI 75 A RAC IA.D
Description: Laufmittel: n-Heptan/EtOH 7:3 Die Probe ist DCM/LM gelöst.

Injection date: 8/28/2014 2:16:06 PM
Acq. Analysis method: CHIRALPAKIARNP.M

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

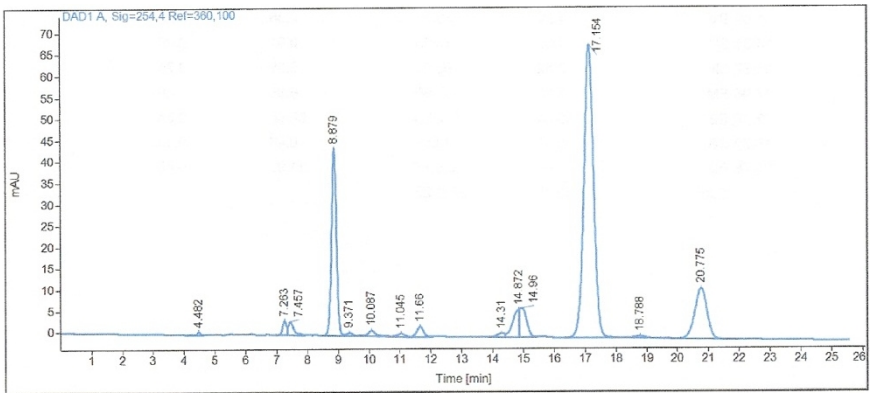
Pressure at start: 43 bar Start flow: 0.700 ml/min Column oven: 30 °C



Name Ni 75 a rac

RT [min]	Type	Area%	Area	Height	Width [min]
6.81	VV	0.39	103.77	12.43	0.13
7.26	VV	0.38	101.97	9.24	0.16
8.88	BB	0.86	230.10	20.48	0.17
11.67	BV	0.78	210.08	14.21	0.23
15.01	VB	48.66	13052.96	678.87	0.30
17.13	BV	48.15	12915.85	586.07	0.34
20.76	BB	0.78	208.35	7.64	0.42
	Sum	100.00	26823.08		

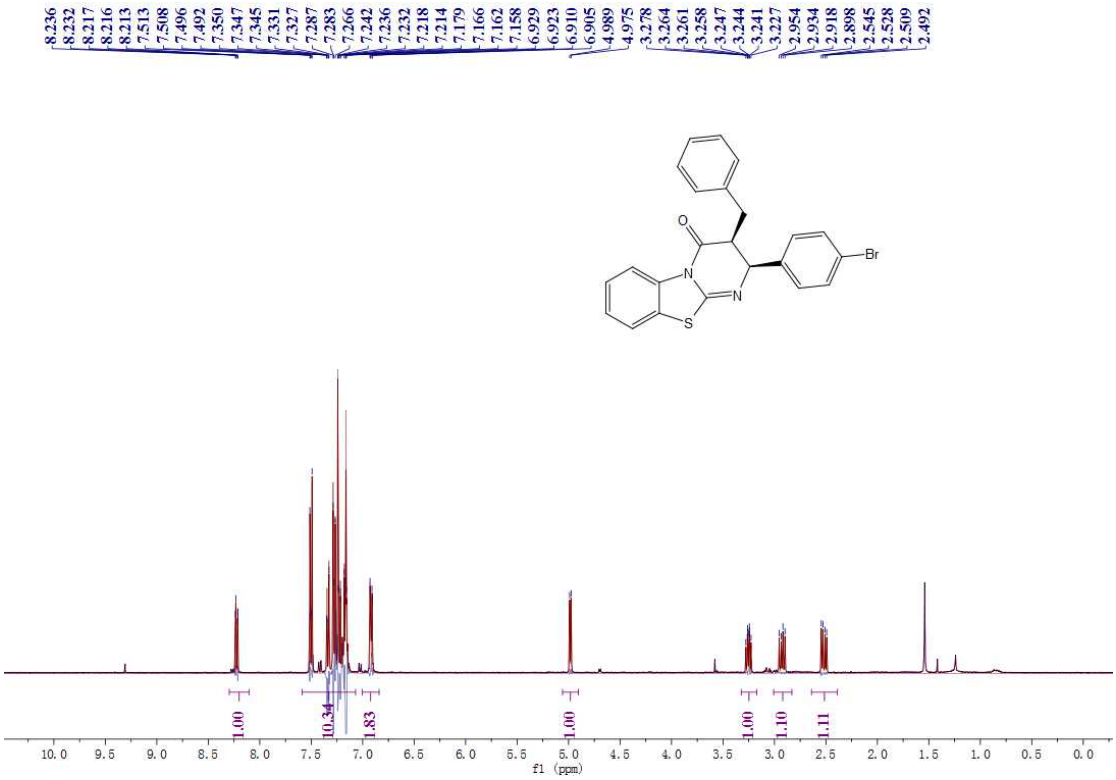
Enantioenriched **3c**



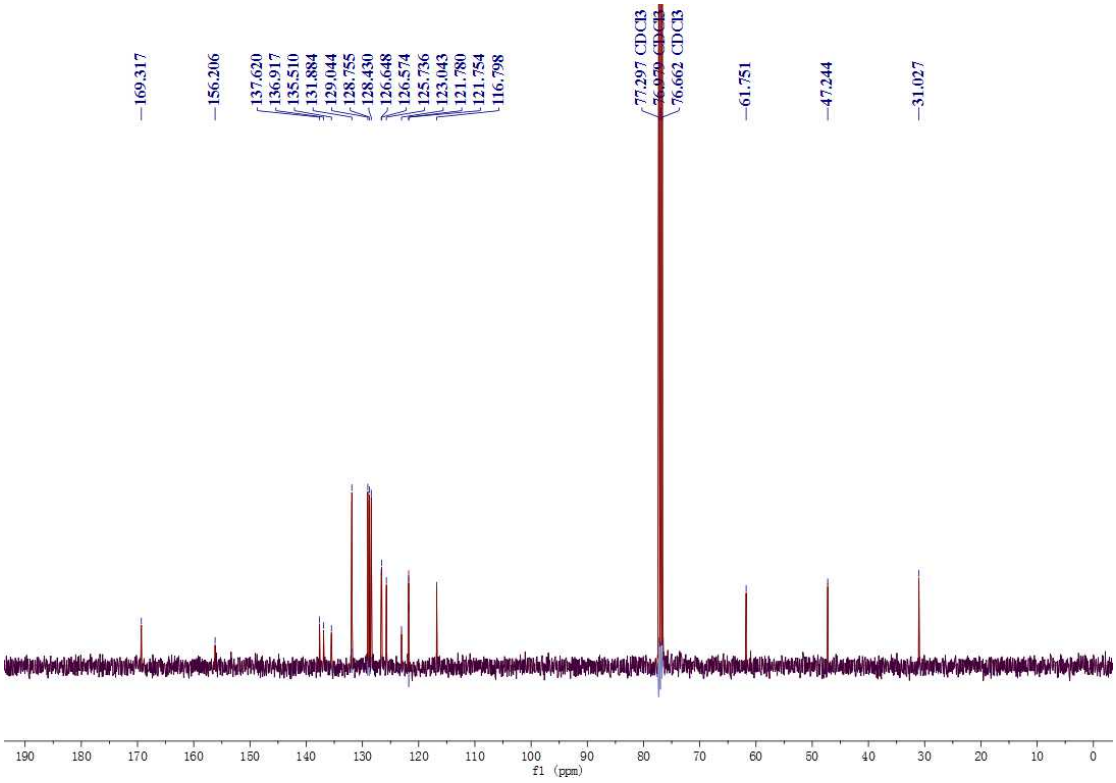
ame Ni 75 b

RT [min]	Type	Area%	Area	Height	Width [min]
4.48	BV	0.33	9.07	0.73	0.17
7.26	BV	1.09	29.71	3.29	0.14
7.46	VV	1.49	40.63	3.16	0.19
8.88	BV	17.80	486.18	43.81	0.17
9.37	VV	0.36	9.70	0.74	0.20
10.09	VV	0.92	25.03	1.33	0.27
11.05	VB	0.41	11.24	0.68	0.25
11.66	BV	1.29	35.23	2.36	0.23
14.31	BV	0.57	15.63	0.91	0.26
14.87	MF	3.52	96.04	6.55	0.24
14.96	FM	3.95	107.99	6.86	0.26
17.15	BB	55.84	1525.20	68.60	0.34
18.79	BB	0.51	13.80	0.46	0.43
20.78	BB	11.93	325.77	11.93	0.43
	Sum	100.00	2731.22		

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



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



HPLC analysis: rac-**3d**

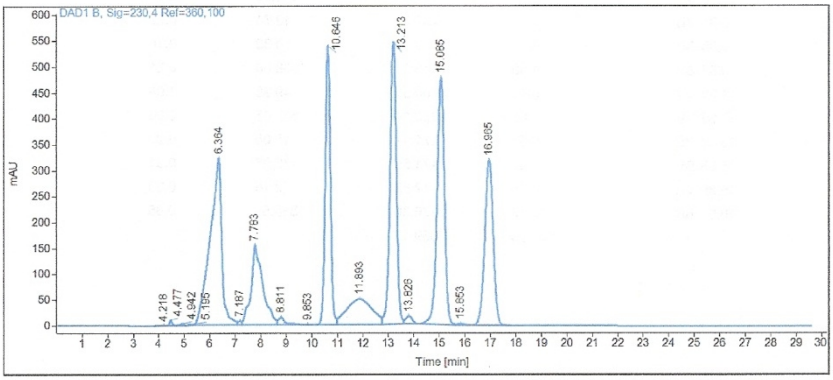
Sample name: **Ni 76 a rac**

Data file: C:\SNOOPY\NI\NI 76 A RAC IA.D
Description: Laufmittel: n-Heptan/EtOH 7:3 Die Probe ist DCM/LM gelöst.

Injection date: 8/14/2014 2:29:12 PM
Acq. Analysis method: CHIRALPAKIARNP.M

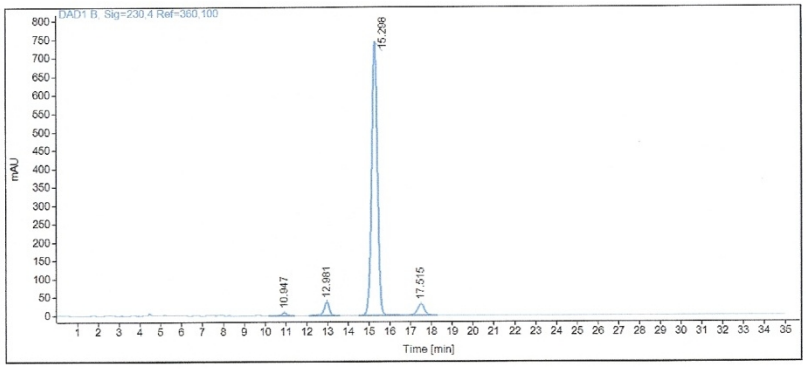
Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

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



RT [min]	Type	Area%	Area	Height	Width [min]
4.22	BV	0.02	9.85	0.85	0.18
4.48	VV	0.15	80.04	10.98	0.11
4.94	VB	0.08	40.60	4.26	0.13
5.19	BB	0.03	15.47	2.78	0.09
6.36	BV	19.54	10359.40	322.88	0.41
7.19	VV	0.14	71.67	7.01	0.15
7.78	VV	9.27	4911.40	154.02	0.41
8.81	VB	0.51	267.86	13.74	0.27
9.85	BB	0.01	3.58	0.33	0.18
10.65	BV	14.05	7448.01	538.86	0.21
11.89	VV	6.41	3400.31	49.28	1.08
13.21	VV	17.62	9339.14	545.05	0.26
13.83	VB	0.51	271.11	15.05	0.27
15.08	BV	17.87	9471.59	476.67	0.31
15.85	VB	0.08	42.82	2.16	0.30
16.97	BB	13.73	7276.30	318.59	0.35
	Sum	100.00	53009.15		

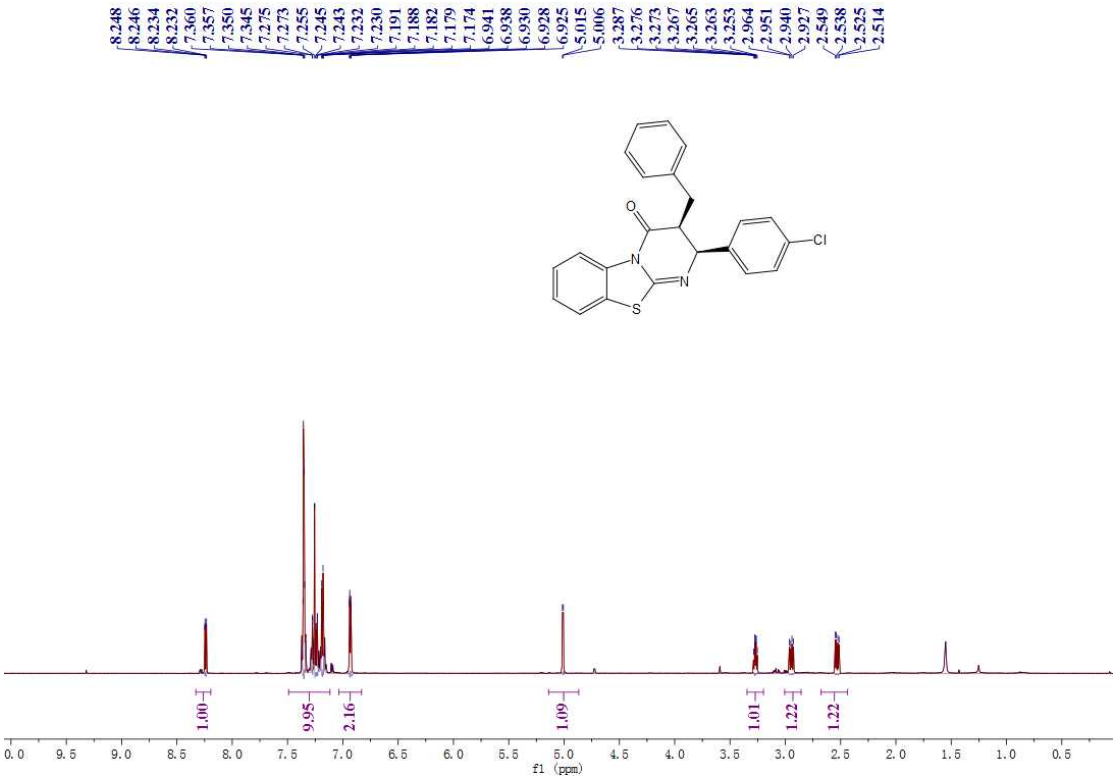
Enantioenriched **3d**



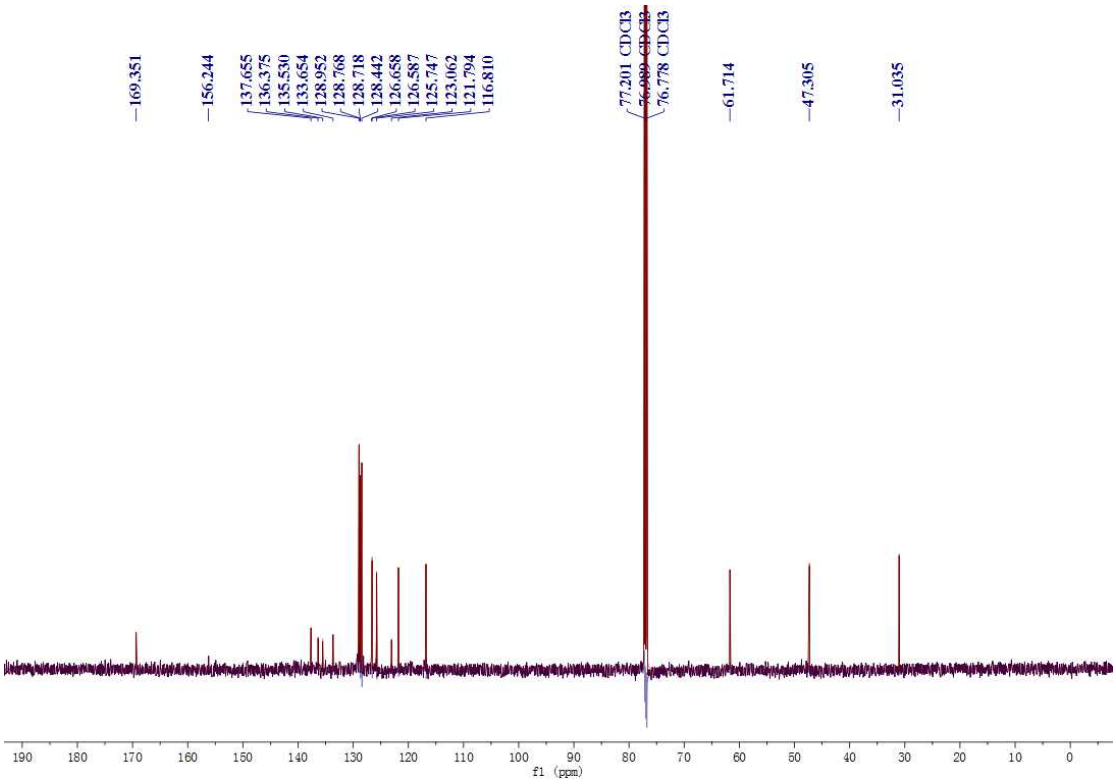
Name Ni 76 b

RT [min]	Type	Area%	Area	Height	Width [min]
10.95	BB	0.67	106.96	7.62	0.22
12.98	BB	4.05	645.84	36.73	0.27
15.30	BB	90.93	14487.28	744.18	0.30
17.51	BB	4.34	691.59	30.10	0.35
	Sum	100.00	15931.67		

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



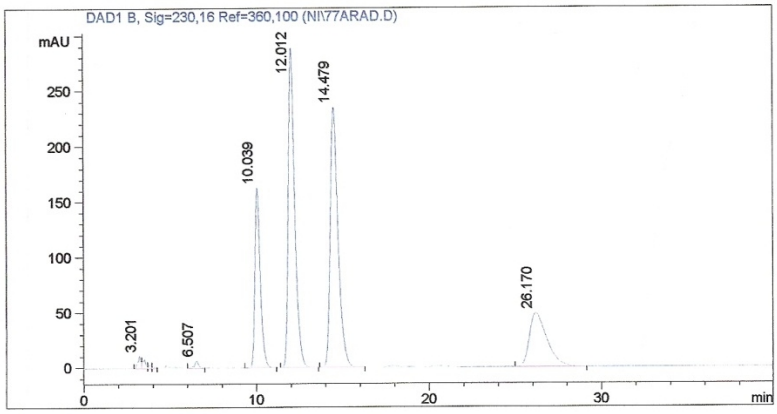
^{13}C NMR of **3e**



HPLC analysis: rac-**3e**

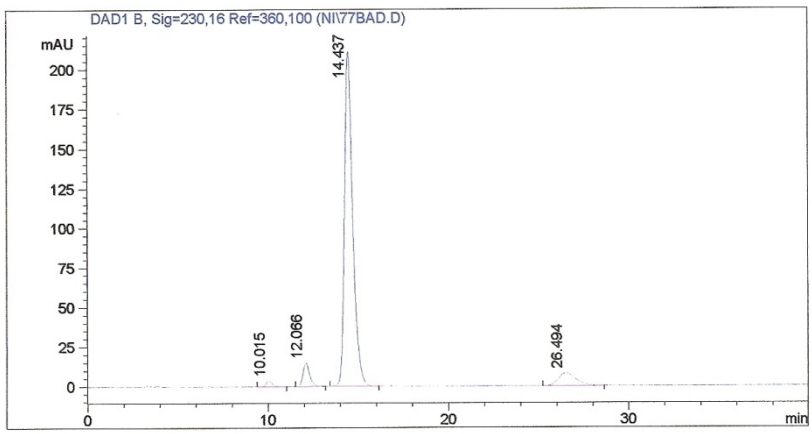
Sample Name:	Ni 77 a rac
Data file:	D:\GONZO\NI\77ARAD.D
Sample Info:	Laufmittel: n-Heptan/IP 9:1; Die Probe ist in DCM/LM gelöst.
Säule:	DAICELAD.M
Säuleninfo:	Chiralpak AD (250x4,6)mm
Operator:	Analytik Labor AKEN
Injektion Time:	10:48:37
Injektion Date:	21.08.2014

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	25.8	26.3
Flow in ml/min:	1.00	1.00



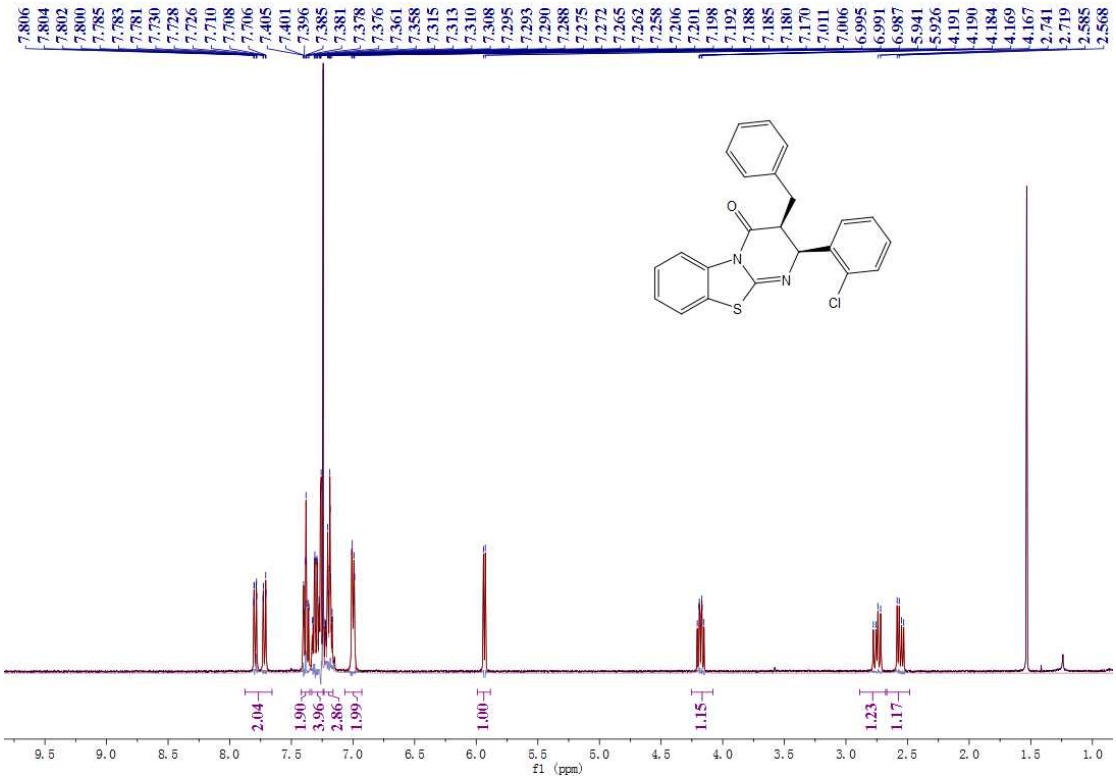
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.20	0.18	10.98	141.85	0.64
2	3.47	0.17	8.20	103.18	0.46
3	3.80	0.15	3.21	30.98	0.14
4	4.00	0.14	1.98	19.57	0.09
5	6.51	0.24	6.59	112.04	0.50
6	10.04	0.32	162.47	3519.73	15.79
7	12.01	0.39	288.53	7475.61	33.54
8	14.48	0.48	234.62	7422.56	33.30
9	26.17	1.09	48.56	3461.63	15.53
Total				22287.13	100.00

Enantioenriched **3e**

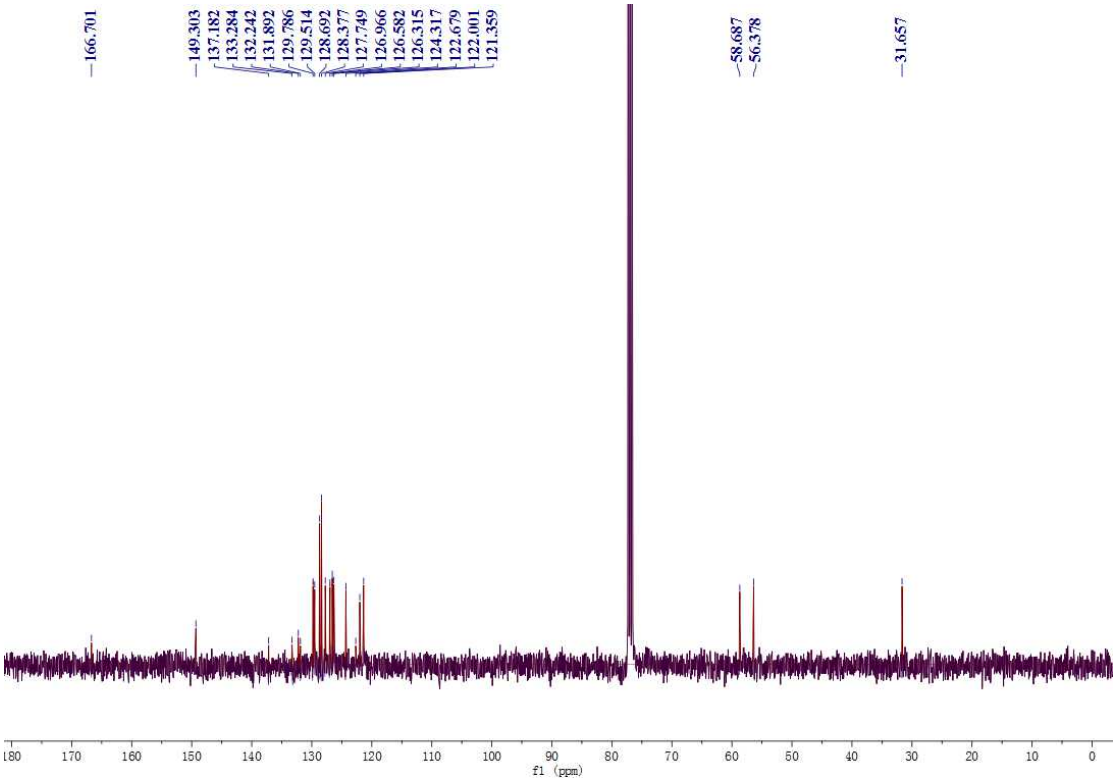


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	10.01	0.34	3.68	84.05	1.09
2	12.07	0.39	14.90	386.22	4.99
3	14.44	0.48	211.29	6714.22	86.79
4	26.49	1.05	8.07	551.93	7.13
Total				7736.42	100.00

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



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



HPLC analysis: rac-**3f**

Agilent Technologies

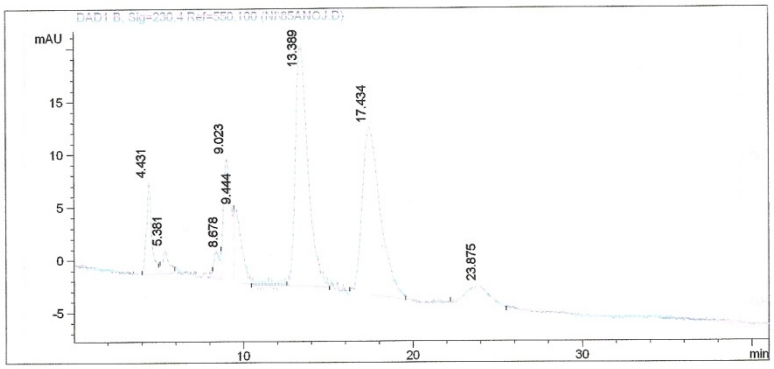
Sample Name: Ni 85 a neu
Data file: D:\BERT\NI\85ANOJ.D
Sample Info: Laufmittel: n-Heptan/EtOH 7:3;
Die Probe ist in DCM/LM gelöst

Säule: DAICELOJ.M
Säuleninfo: Chiralcel OJ (250x4,6)mm

Operator: Analytik Labor AKEN

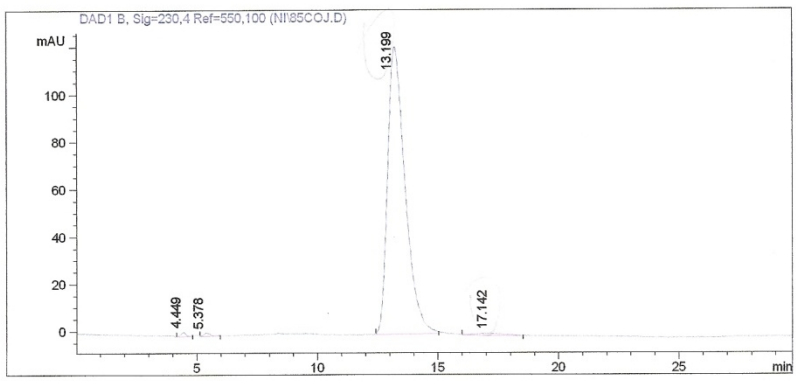
Injektion Time: 09:58:41
Injektion Date: 17.09.2014

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	33.5	33.1
Flow in ml/min:	0.7	0.7



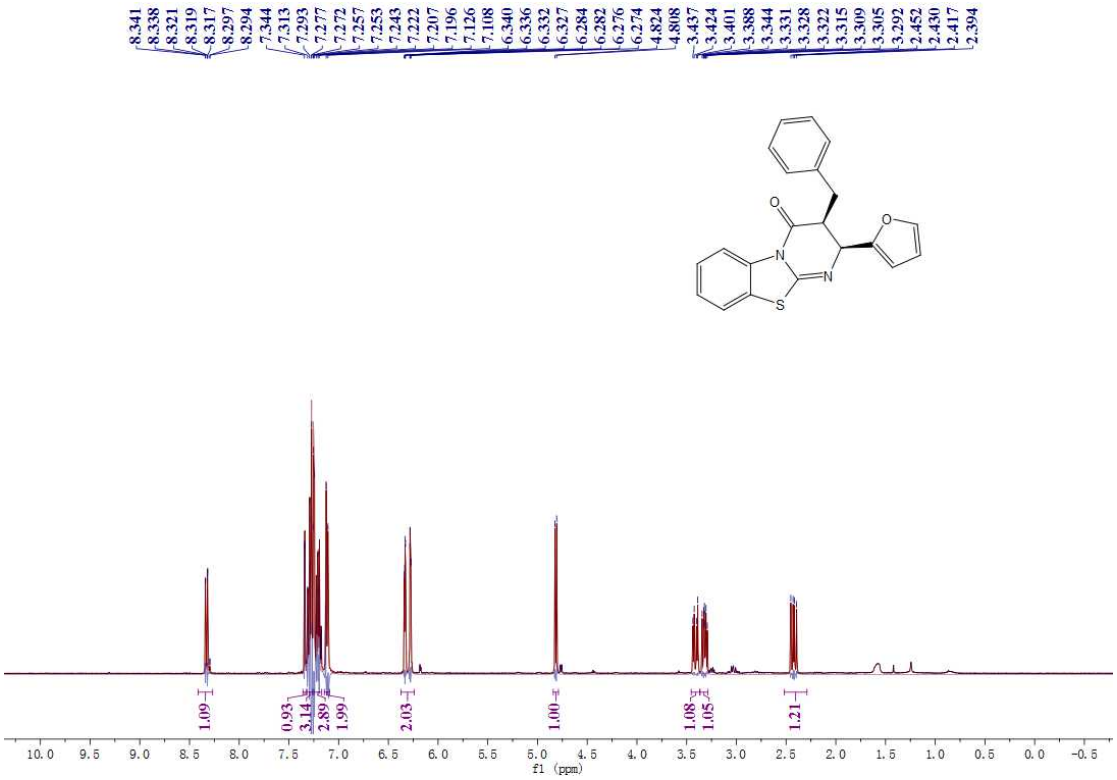
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.43	0.30	8.76	189.27	5.59
2	5.38	0.36	2.27	59.68	1.76
3	8.68	0.40	2.65	63.18	1.87
4	9.02	0.52	11.58	361.97	10.69
5	9.44	0.49	6.95	204.42	6.04
6	13.39	0.86	22.85	1174.67	34.69
7	17.43	0.99	15.88	1176.42	34.74
8	23.87	1.43	1.82	156.94	4.63
Total				3386.55	100.00

Enantioenriched **3f**

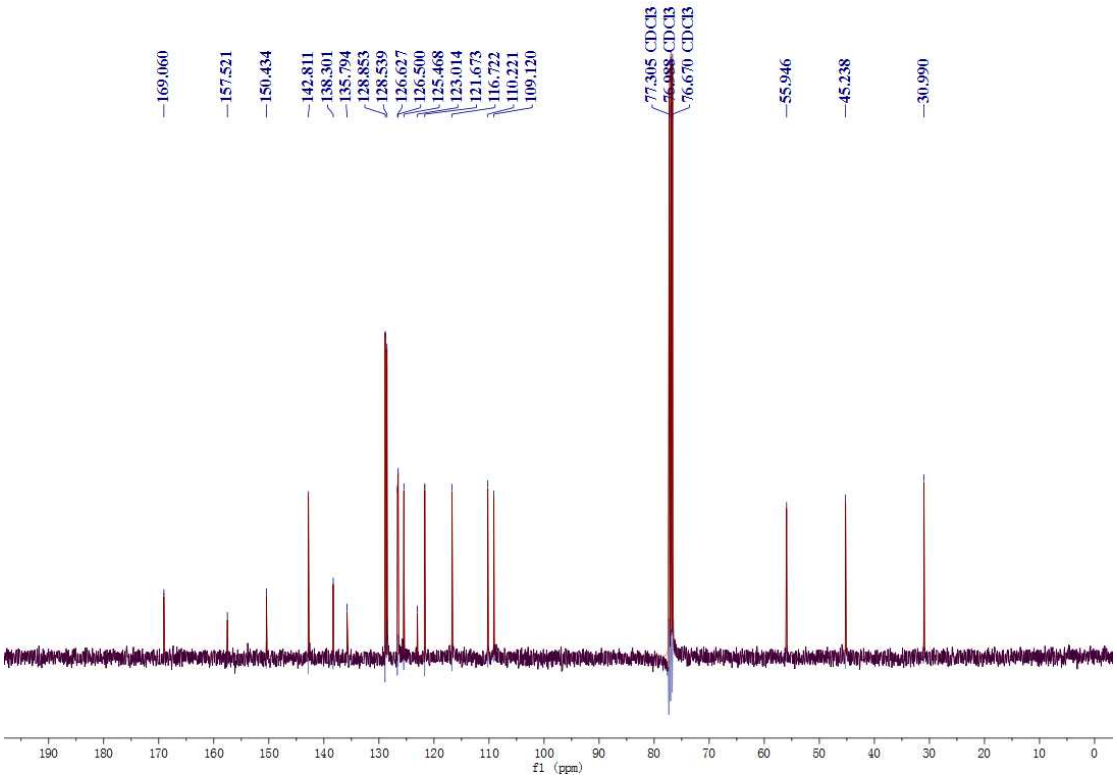


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.45	0.24	1.81	31.54	0.50
2	5.38	0.27	1.30	24.29	0.39
3	13.20	0.75	121.34	6140.56	97.85
4	17.14	1.31	1.00	78.95	1.26
Total				6275.34	100.00

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

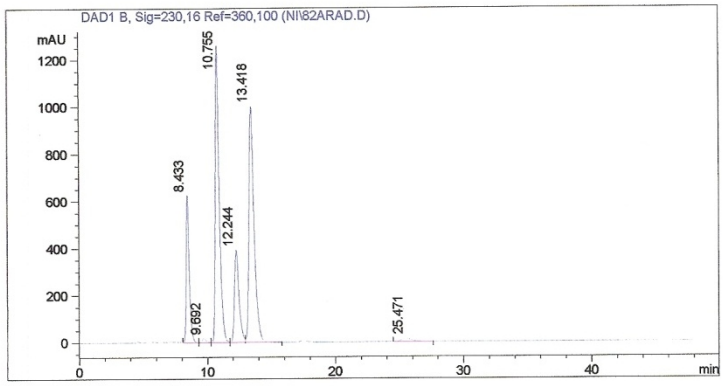


^{13}C NMR of **3g**



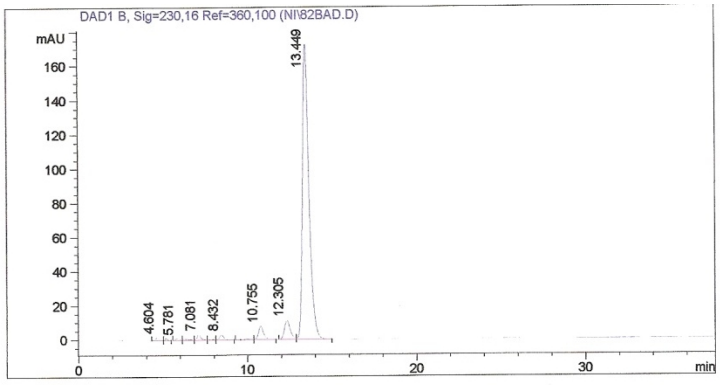
HPLC analysis: rac-**3g**

```
Sample Name:          Ni 82 a rac
Data file:            D:\GONZO\NI\82ARAD.D
Sample Info:          Laufmittel: n-Heptan/EtOH 7:3
                      Die Probe ist in LM/DCM gelöst

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

Injektion Time:       19:18:56
Injektion Date:       25.08.2014

Instrument Conditions:   At Start          At Stop
Temperature in°C:          30.0°C            30.0°C
Pressure in bar:           22.1              22.5
Flow in ml/min:            0.70              0.70
```



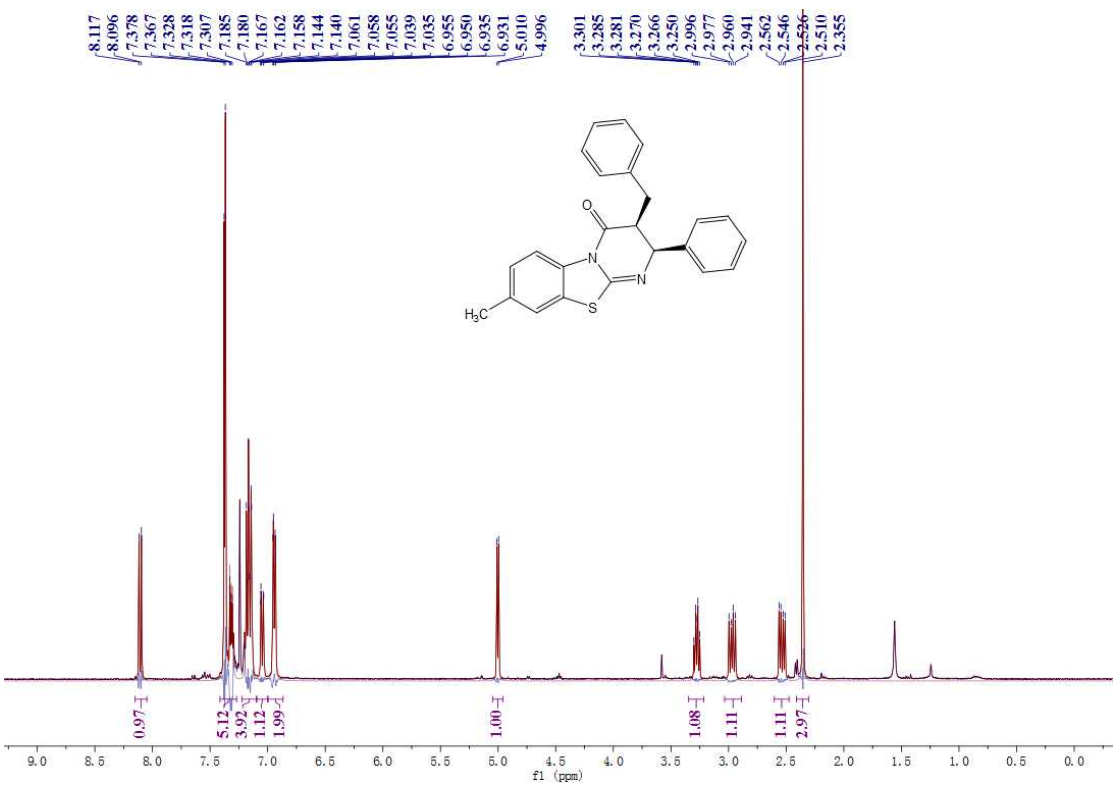
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.43	0.24	625.92	10228.92	13.42
2	9.69	0.33	17.14	397.80	0.52
3	10.75	0.32	1260.34	27133.10	35.59
4	12.24	0.37	392.53	9759.25	12.80
5	13.42	0.42	1001.63	27954.02	36.67
6	25.47	0.77	14.87	764.42	1.00
Total				76237.51	100.00

Enantioenriched **3g**

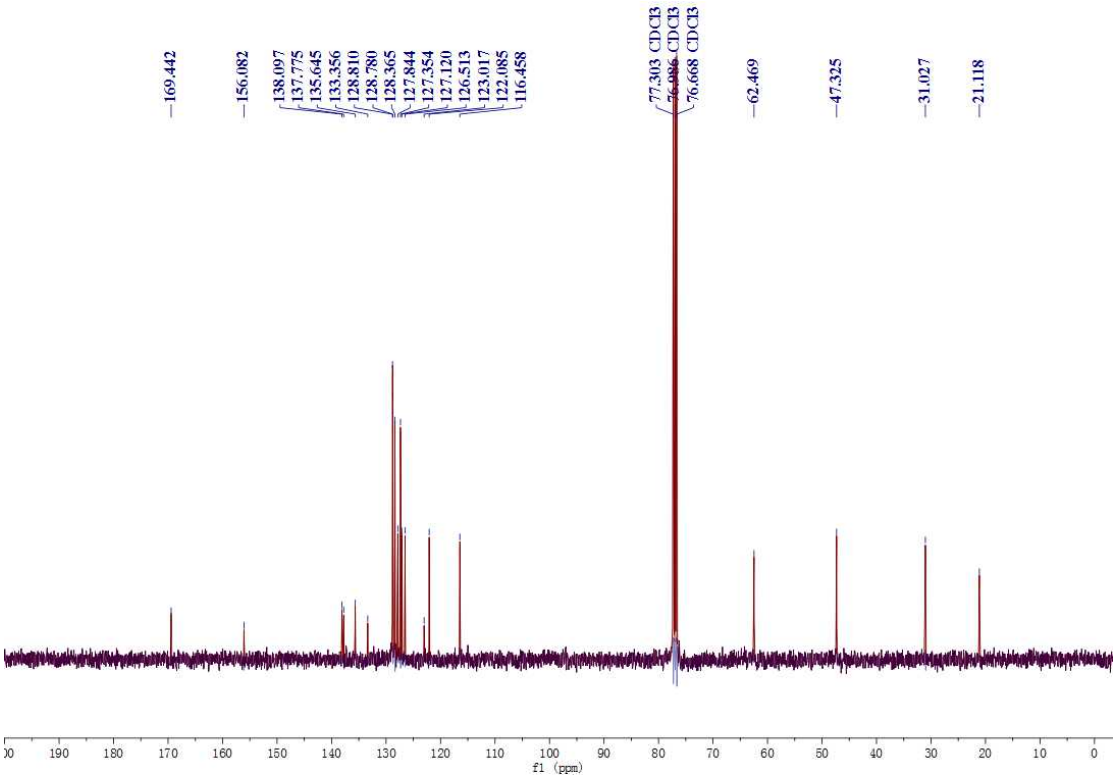


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.60	0.22	1.55	25.17	0.48
2	5.15	0.16	1.27	13.81	0.26
3	5.78	0.22	0.99	15.59	0.30
4	6.31	0.32	0.60	14.58	0.28
5	7.08	0.22	3.38	50.83	0.96
6	7.95	0.35	0.27	7.09	0.13
7	8.43	0.27	3.12	56.33	1.07
8	10.00	0.52	0.47	18.65	0.35
9	10.75	0.32	7.96	167.92	3.19
10	12.30	0.37	11.38	273.58	5.19
11	13.45	0.41	172.62	4626.01	87.79
Total				5269.56	100.00

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



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



HPLC analysis: rac-**3h**

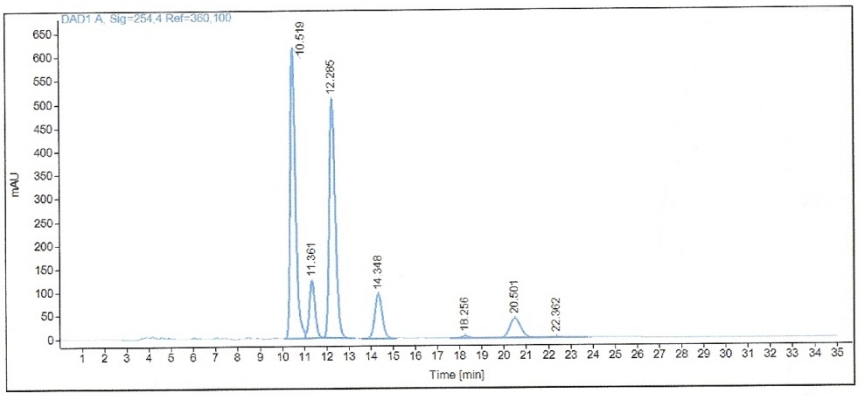
Sample name: **Ni 80 a rac**

Data file: C:\SNOOPY\NI\NI 80 A RAC 1IC.D
Description: Laufmittel: n-Heptan/IP 9:1 Die Probe ist DCM/LM gelöst.

Injection date: 8/25/2014 2:05:07 PM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

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

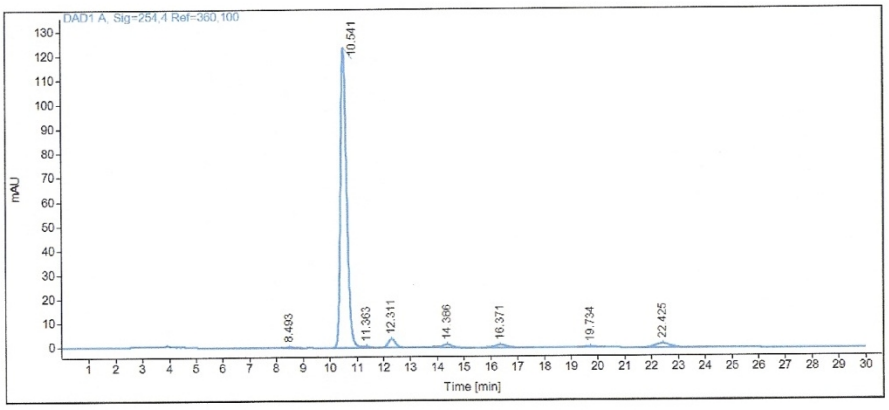
Pressure at start: 22 bar Start flow: 0.500 ml/min Column oven: 30 °C



Name Ni 80 a rac

RT [min]	Type	Area%	Area	Height	Width [min]
10.52	BV	39.27	10178.03	618.48	0.25
11.36	VB	8.43	2185.63	122.66	0.28
12.29	BB	37.32	9672.71	508.46	0.29
14.35	BV	8.45	2190.20	94.89	0.36
18.26	BB	0.50	128.51	4.12	0.48
20.50	BV	5.67	1468.64	41.65	0.54
22.36	VB	0.36	93.18	2.37	0.60
	Sum	100.00	25916.89		

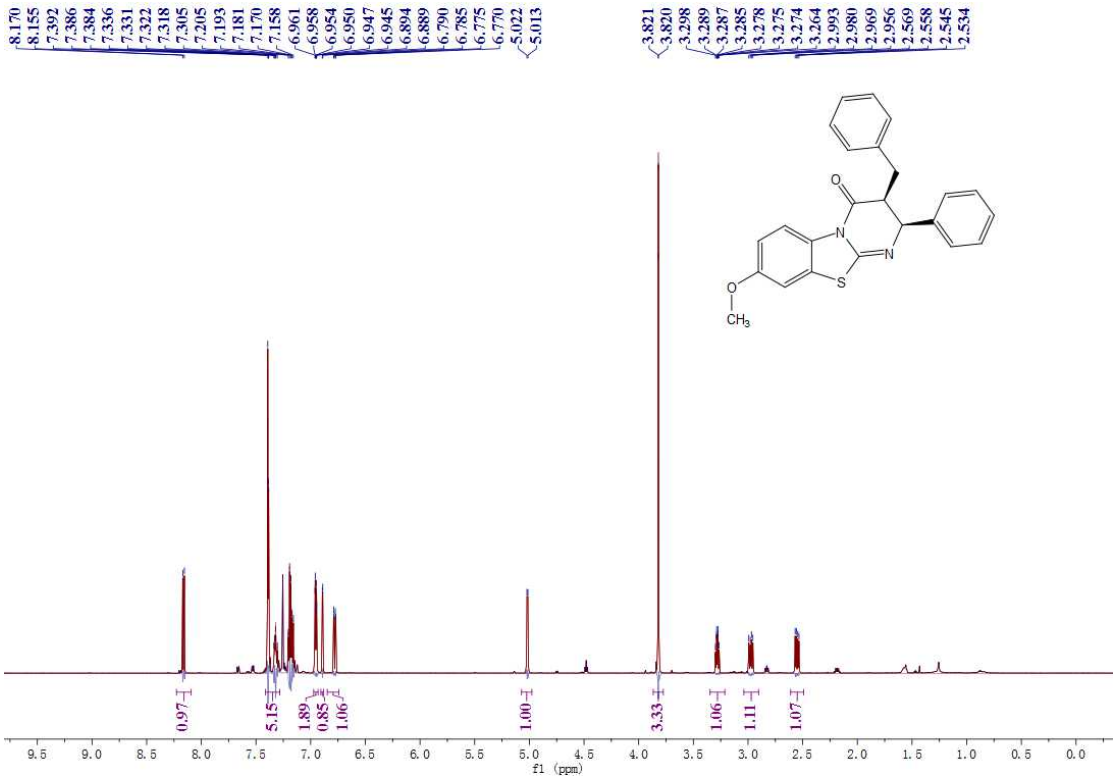
Enantioenriched **3h**



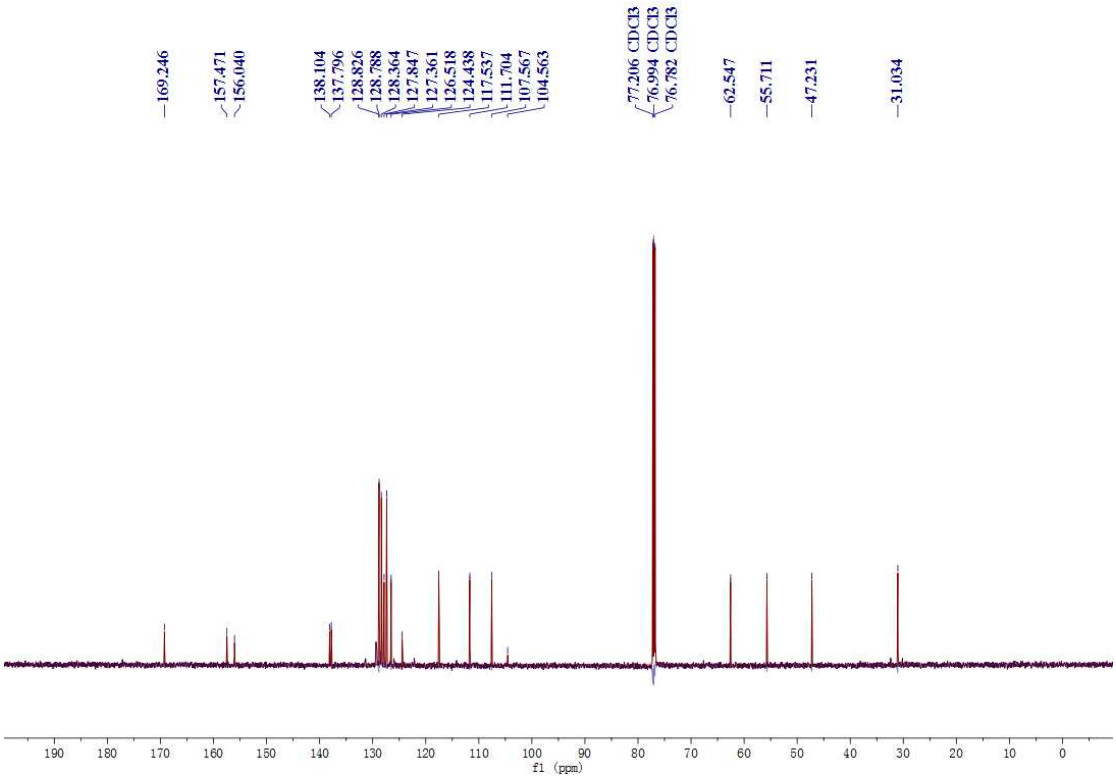
Name Ni 80 b

RT [min]	Type	Area%	Area	Height	Width [min]
8.49	BB	0.25	5.70	0.45	0.19
10.54	BV	89.02	1991.12	123.65	0.25
11.36	VV	0.51	11.40	0.56	0.30
12.31	VB	3.26	72.95	3.62	0.31
14.39	BB	1.74	38.82	1.34	0.42
16.37	BB	1.75	39.10	1.21	0.47
19.73	BB	0.56	12.47	0.46	0.43
22.43	BB	2.91	65.17	1.66	0.60
	Sum	100.00	2236.74		

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

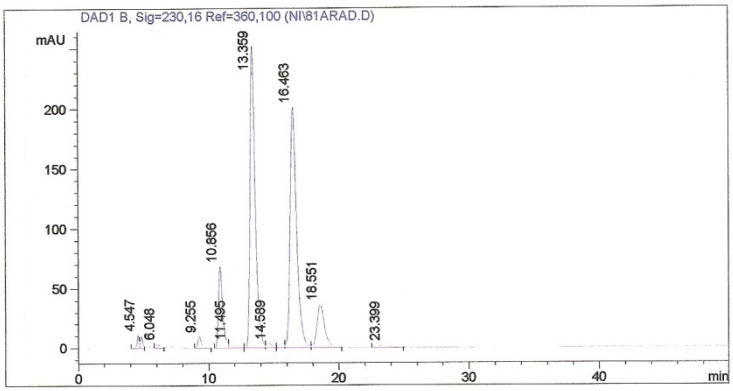


^{13}C NMR of **3i**



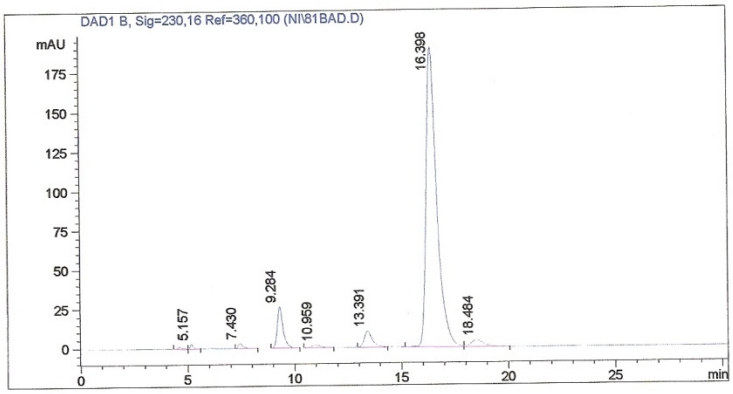
HPLC analysis: rac-**3i**

```
Sample Name:          Ni 81 a rac
Data file:            D:\GONZO\NI\81ARAD.D
Sample Info:          Laufmittel: n-Heptan/EtOH 7:3
                      Die Probe ist in LM/DCM gelöst

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

Injektion Time:       18:27:45
Injektion Date:       25.08.2014

Instrument Conditions:   At Start          At Stop
Temperature in°C:          30.0°C            30.0°C
Pressure in bar:           21.9              22.9
Flow in ml/min:            0.70              0.70
```



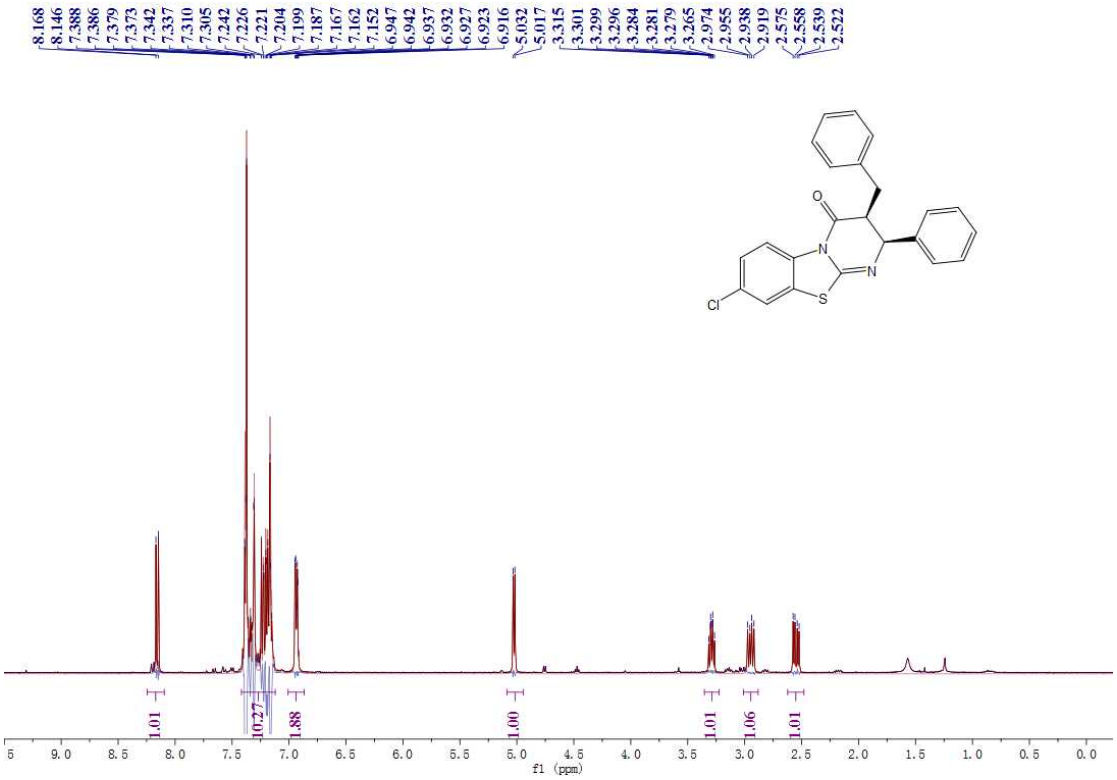
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.55	0.16	11.16	123.89	0.69
2	4.80	0.19	10.05	128.44	0.71
3	6.05	0.29	3.87	77.36	0.43
4	9.26	0.30	9.70	193.23	1.07
5	10.86	0.37	68.54	1540.84	8.57
6	11.50	0.46	3.66	100.57	0.56
7	13.36	0.41	252.27	6948.46	38.63
8	14.59	0.44	3.96	116.86	0.65
9	15.64	0.38	3.62	89.35	0.50
10	16.46	0.53	201.23	7081.27	39.37
11	18.55	0.61	36.66	1473.66	8.19
12	23.40	0.77	2.11	111.49	0.62
Total				17985.41	100.00

Enantioenriched **3i**

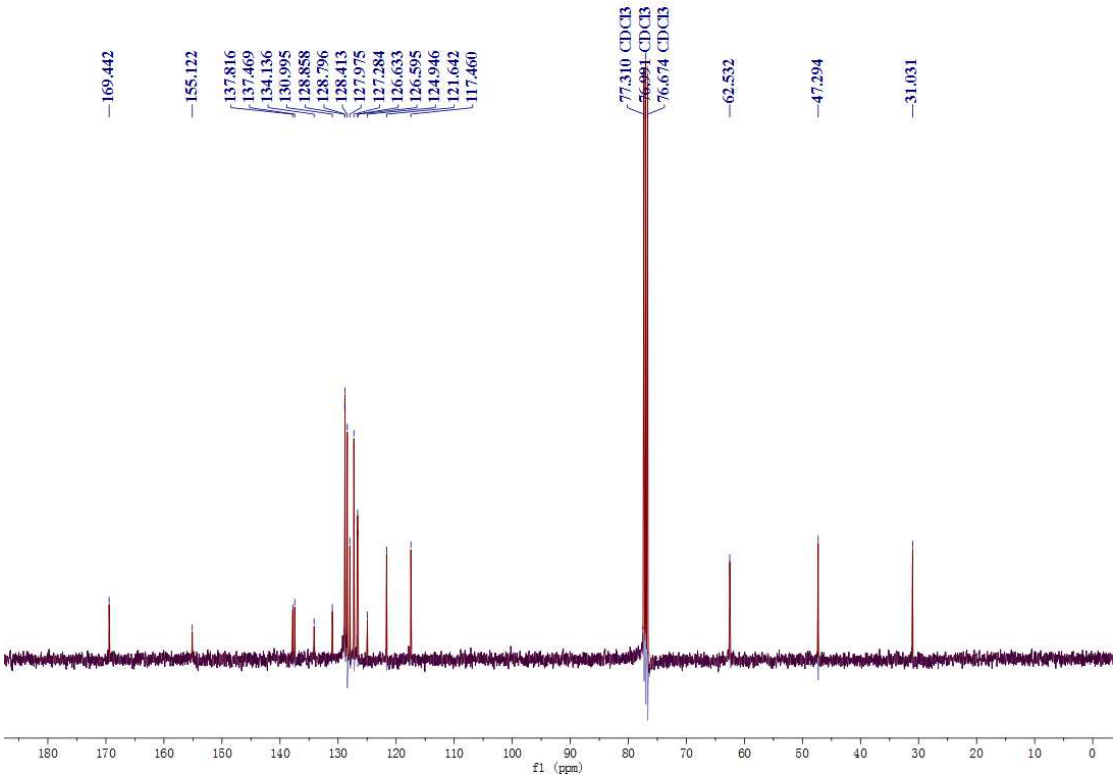


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.61	0.25	1.53	28.73	0.37
2	5.16	0.16	3.32	36.66	0.48
3	7.43	0.22	3.22	47.76	0.62
4	9.28	0.28	26.35	495.07	6.41
5	10.96	0.49	1.64	50.74	0.66
6	13.39	0.41	10.39	284.26	3.68
7	16.40	0.52	190.29	6591.13	85.40
8	18.48	0.60	4.57	183.66	2.38
Total				7718.02	100.00

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



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



HPLC analysis: rac-**3j**

Sample name: **NI 78a**

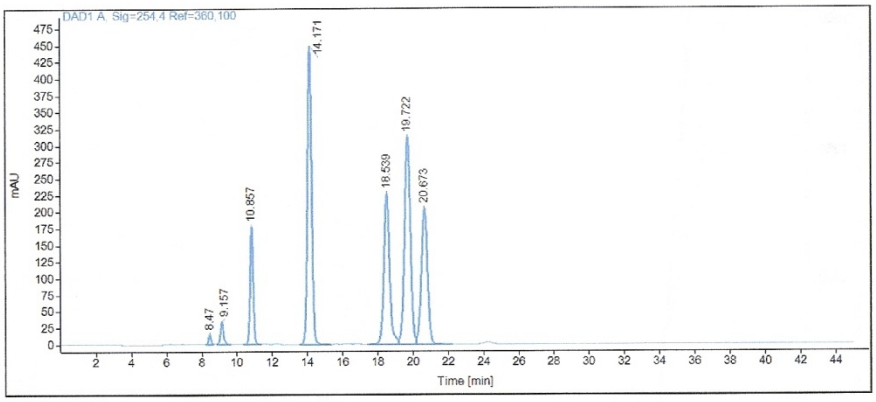
Data file: C:\SNOOPY\NI\78AR1IA.D
Description: Laufmittel: n-Heptan/EtOH 7:3; Probe ist in LM/DCM gelöst.

Injection date: 8/22/2014 2:10:35 PM

Acq. Analysis method: CHIRALPAKIARNP.M

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

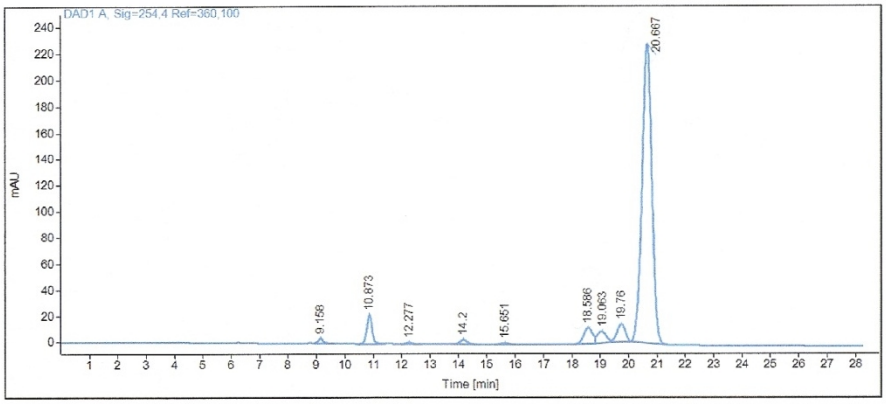
Pressure at start: 30 bar Start flow: 0.500 ml/min Column oven: 29.97 °C



Name NI 78a

RT [min]	Type	Area%	Area	Height	Width [min]
8.47	VV	0.51	139.45	14.96	0.14
9.16	VB	1.55	425.39	34.83	0.18
10.86	BV	8.01	2204.42	178.13	0.19
14.17	BB	26.70	7345.37	448.61	0.25
18.54	BV	18.79	5169.10	226.69	0.35
19.72	VV	26.37	7253.87	312.78	0.36
20.67	VB	18.07	4971.92	204.59	0.38
	Sum	100.00	27509.52		

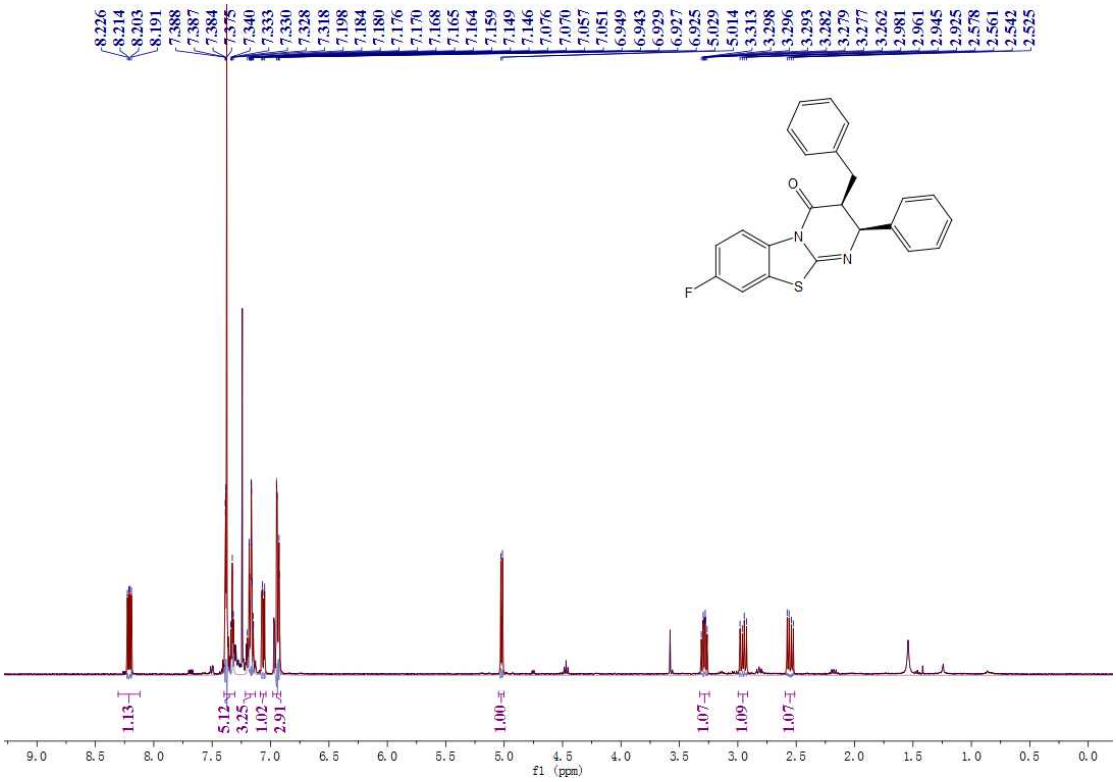
Enantioenriched **3j**



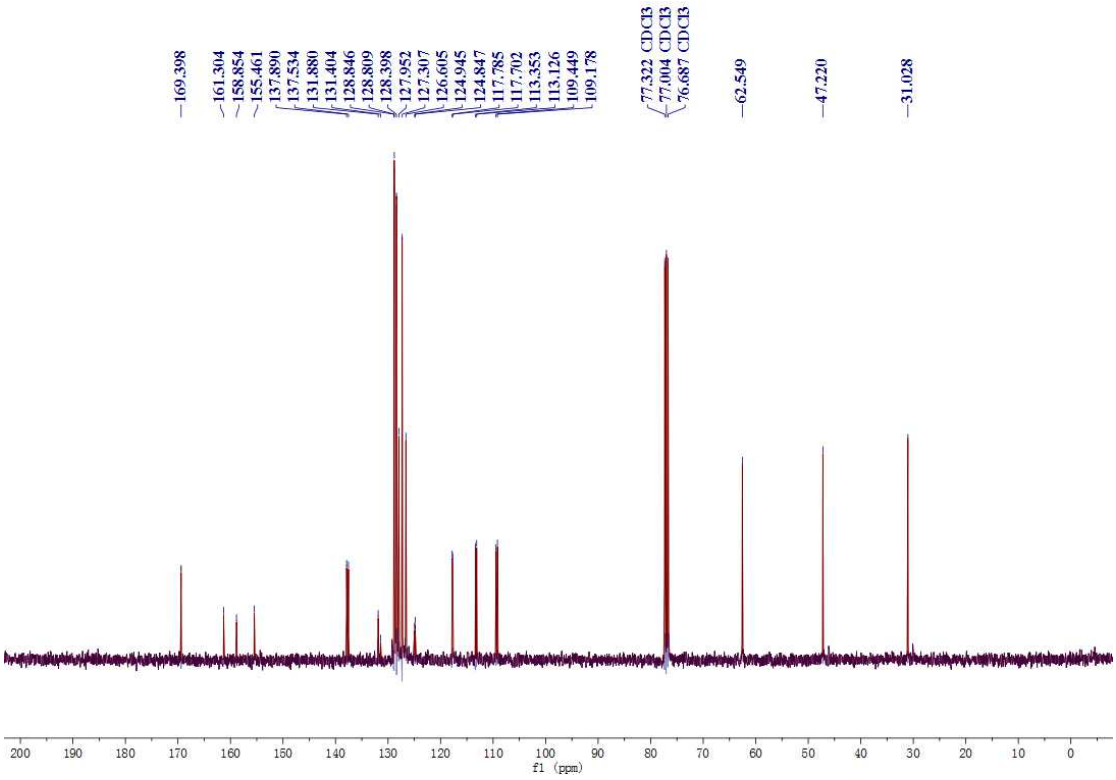
Name Ni 78 b

RT [min]	Type	Area%	Area	Height	Width [min]
9.16	VV	0.76	50.16	3.77	0.19
10.87	BV	4.29	283.19	21.98	0.20
12.28	BB	0.23	15.33	1.14	0.21
14.20	BB	0.88	58.26	3.33	0.27
15.65	BB	0.33	21.47	1.24	0.27
18.59	BV	4.01	264.78	12.11	0.33
19.06	VV	3.01	198.88	8.94	0.34
19.76	VB	4.20	277.37	13.61	0.32
20.67	BB	82.29	5433.83	228.04	0.37
	Sum	100.00	6603.27		

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



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



HPLC analysis: rac-**3k**

Sample name: **Ni 79 a rac**

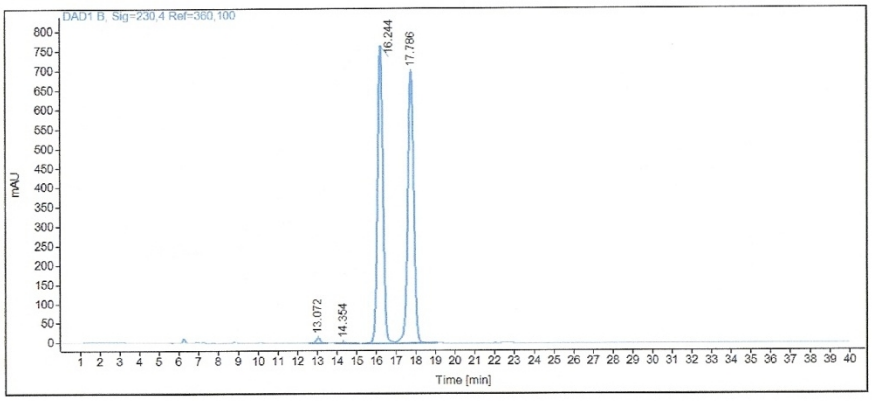
Data file: C:\SNOOPY\NI\79AR2IA.D
Description: Laufmittel: n-Heptan/EtOH 7:3;
Probe ist in LM/DCM gelöst.

Injection date: 8/29/2014 11:32:13 AM

Acq. Analysis method: CHIRALPAKIARNP.M

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

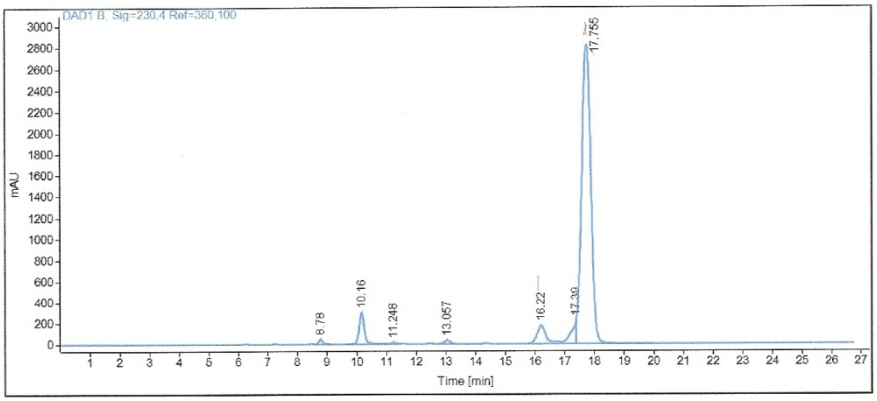
Pressure at start: 31 bar Start flow: 0.500 ml/min Column oven: 29.99 °C



Name Ni 79 a rac

RT [min]	Type	Area%	Area	Height	Width [min]
13.07	BB	0.70	203.93	13.66	0.23
14.35	BB	0.17	49.85	2.78	0.27
16.24	BV	49.31	14467.52	764.91	0.29
17.79	VB	49.82	14618.54	699.14	0.32
	Sum	100.00	29339.84		

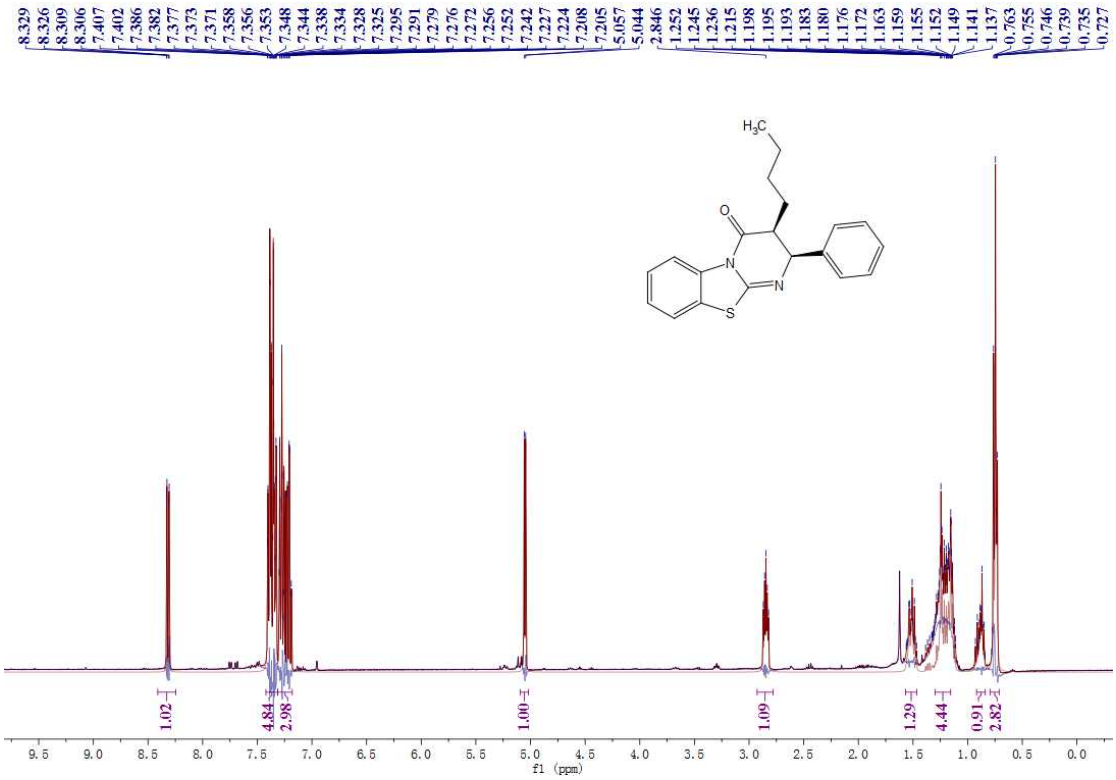
Enantioenriched **3k**



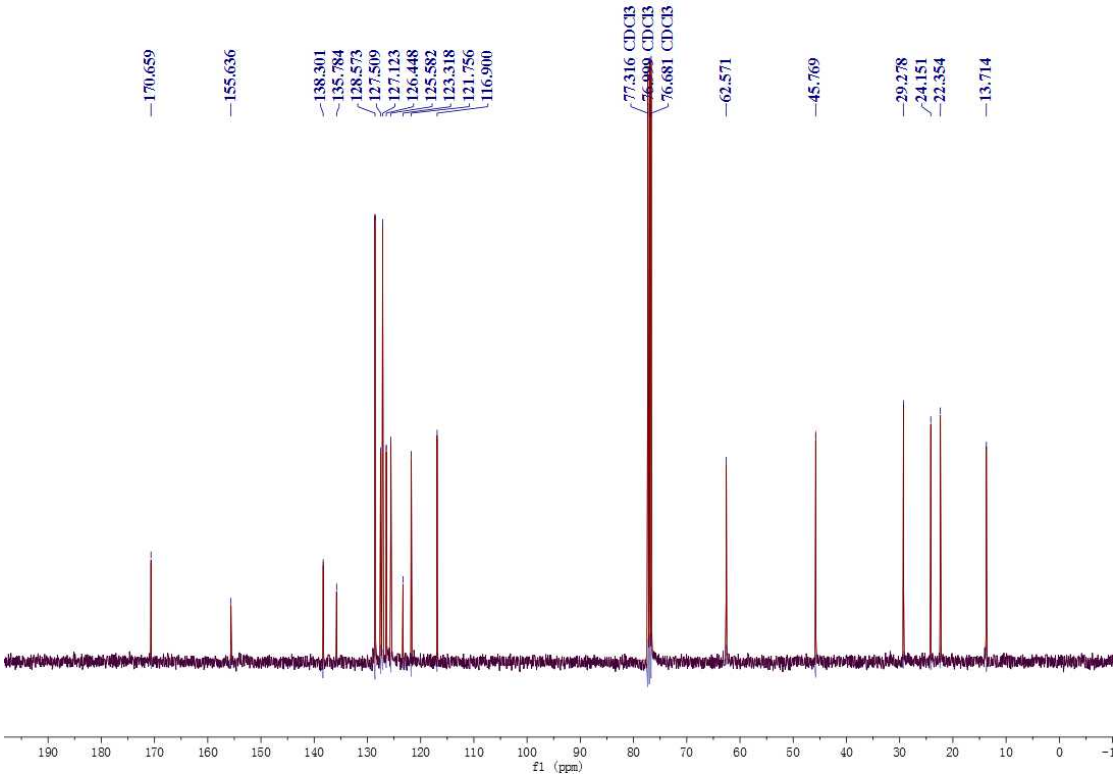
Name Ni 79 b

RT [min]	Type	Area%	Area	Height	Width [min]
8.78	VB	0.66	481.60	44.07	0.16
10.16	BV	5.08	3728.16	296.39	0.19
11.25	VV	0.29	213.46	14.60	0.22
13.06	VB	0.65	475.79	31.37	0.23
16.22	VV	5.01	3678.52	169.07	0.33
17.39	MF	3.41	2504.04	216.62	0.19
17.75	FM	84.91	62351.34	2818.94	0.37
	Sum	100.00	73432.91		

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



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



HPLC analysis: scalemic mixture of **3l** and *ent*-**3l**

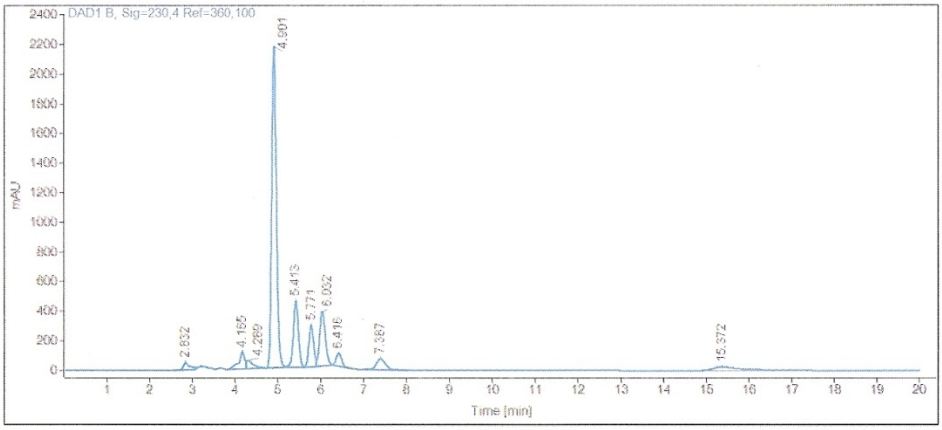
Sample name: Ni 86 b 1+2

Data file: C:\SNOOPY\NI\NI 86 B 1+2 IC.D
Description: Laufmittel: n-Heptan/IP 9:1 Die Probe ist DCM/LM gelöst.

Injection date: 10/1/2014 11:43:41 AM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

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

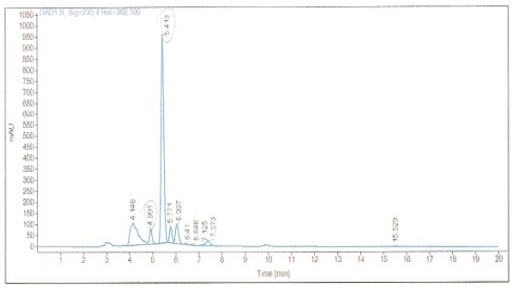
Pressure at start: 23 bar **Start flow:** 0.700 ml/min **Column oven:** 30.01 °C



Name Ni 86 b 1+2

RT [min]	Type	Area%	Area	Height	Width [min]
2.83	BV	1.89	592.49	50.40	0.16
4.16	BV	3.56	1119.69	113.78	0.14
4.29	VB	1.91	600.60	54.86	0.16
4.90	BV	51.82	16286.05	2171.36	0.12
5.41	VB	11.84	3722.13	448.95	0.13
5.77	BV	7.23	2271.81	278.24	0.13
6.03	VB	10.91	3427.03	369.51	0.14
6.42	BB	2.52	792.90	88.40	0.14
7.39	BB	3.65	1146.49	73.78	0.24
15.37	BBA	4.67	1466.05	25.37	0.79
	Sum	100.00	31425.24		

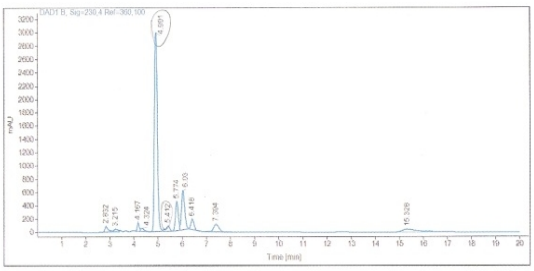
Enantioenriched **3l**



Name Ni 86 - B1

RT [min]	Type	Area%	Area	Height	Width [min]
4.15	BV	19.44	2455.99	99.08	0.31
4.90	VB	4.40	555.98	69.17	0.12
5.41	BB	60.75	7676.68	947.68	0.12
5.77	BV	4.55	575.17	74.37	0.12
6.04	VB	6.59	832.87	88.92	0.15
6.41	BV	0.29	36.80	4.96	0.12
6.65	VB	0.21	25.96	3.21	0.13
7.12	BV	0.30	37.67	4.82	0.13
7.37	VB	2.67	336.87	23.66	0.21
15.53	BBA	0.81	102.35	1.72	0.83
	Sum	100.00	12636.35		

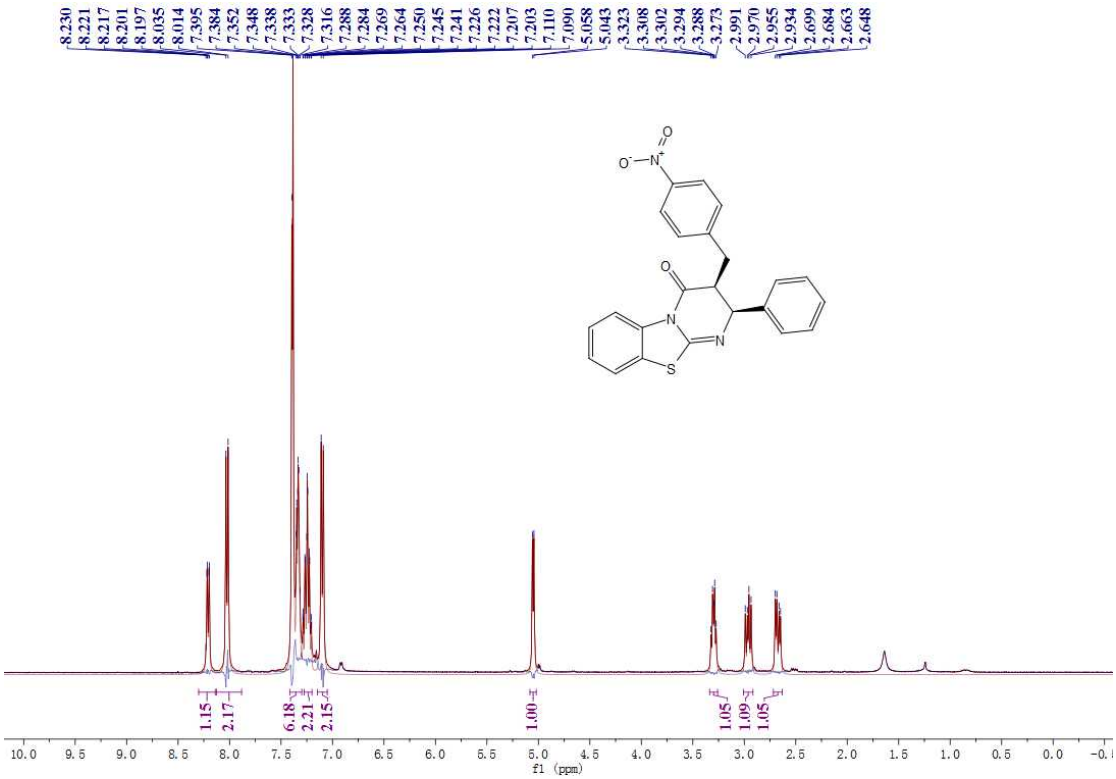
ent-**3l**



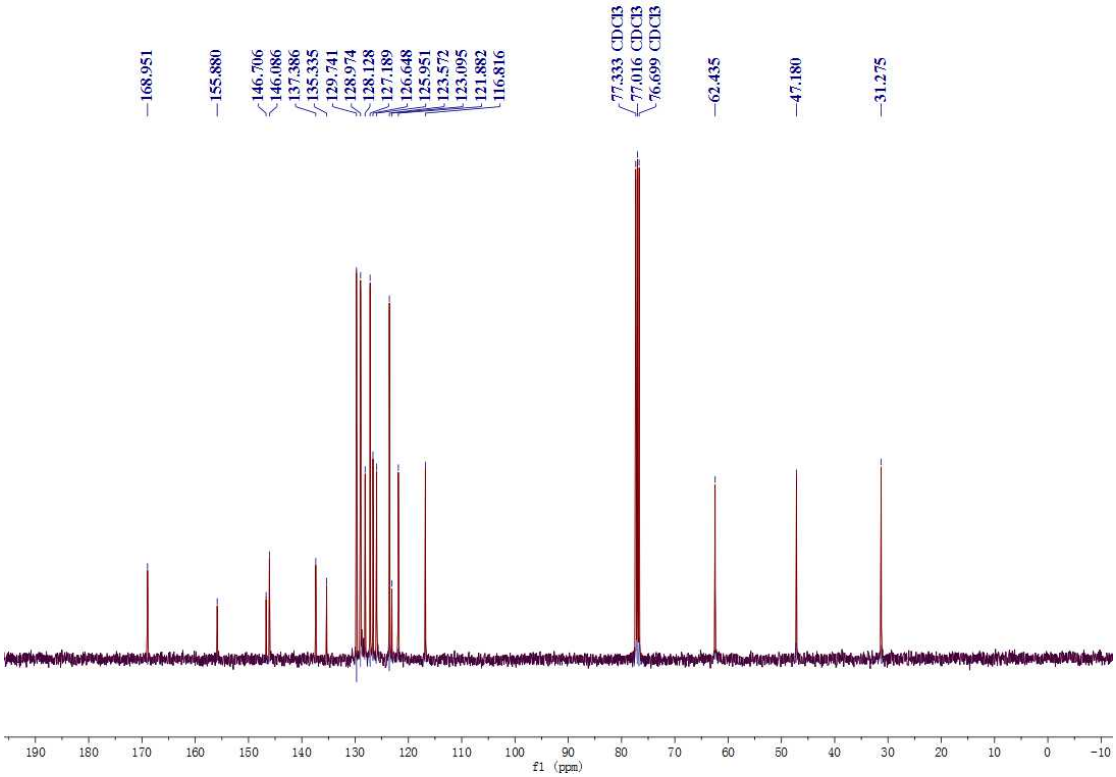
Name Ni 86 - B2

RT [min]	Type	Area%	Area	Height	Width [min]
2.83	BV	1.99	866.73	84.63	0.15
3.21	VV	1.14	496.33	37.24	0.18
4.17	BV	1.63	708.89	126.47	0.09
4.32	VB	0.97	423.66	42.48	0.15
4.90	BV	58.49	25433.26	2986.06	0.14
5.41	VB	2.12	922.02	78.89	0.17
5.77	BV	8.33	3622.00	436.65	0.13
6.03	VB	12.59	5475.42	590.53	0.14
6.42	BB	3.18	1381.26	152.63	0.14
7.39	BB	4.01	1743.86	112.29	0.24
15.33	BBA	5.53	2406.50	43.98	0.75
	Sum	100.00	43479.93		

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



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



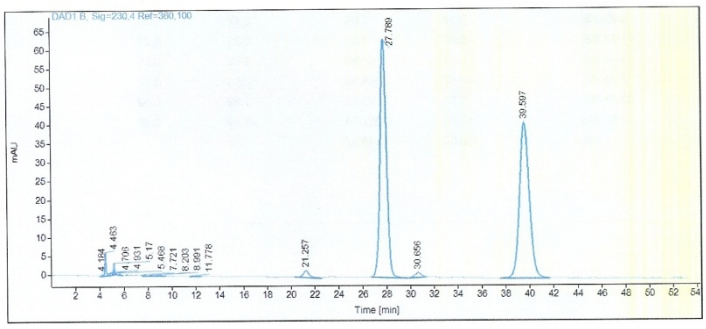
HPLC analysis: rac-**3m**

Sample name: **Ni 87 a rac**
Data file: C:\SNOOPY\NI\NI 87 A RAC IA.D
Description: Laufmittel: n-Heptan/EtOH 7:3 Die Probe ist DCM/LM gelöst.

Injection date: 9/1/2014 8:41:15 AM
Acq. Analysis method: CHIRALPAKIARNP.M

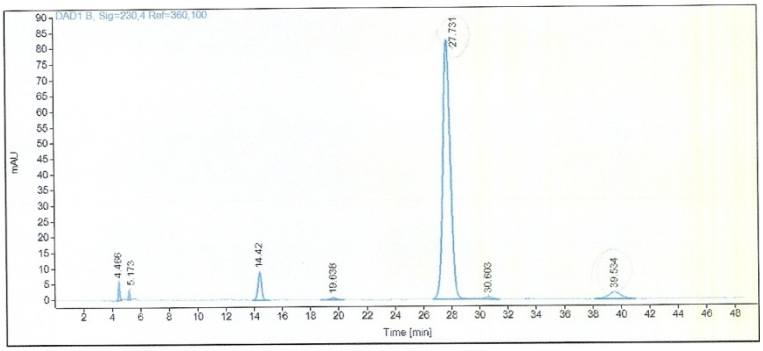
Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 43 bar Start flow: 0.700 ml/min Column oven: 29.99 °C



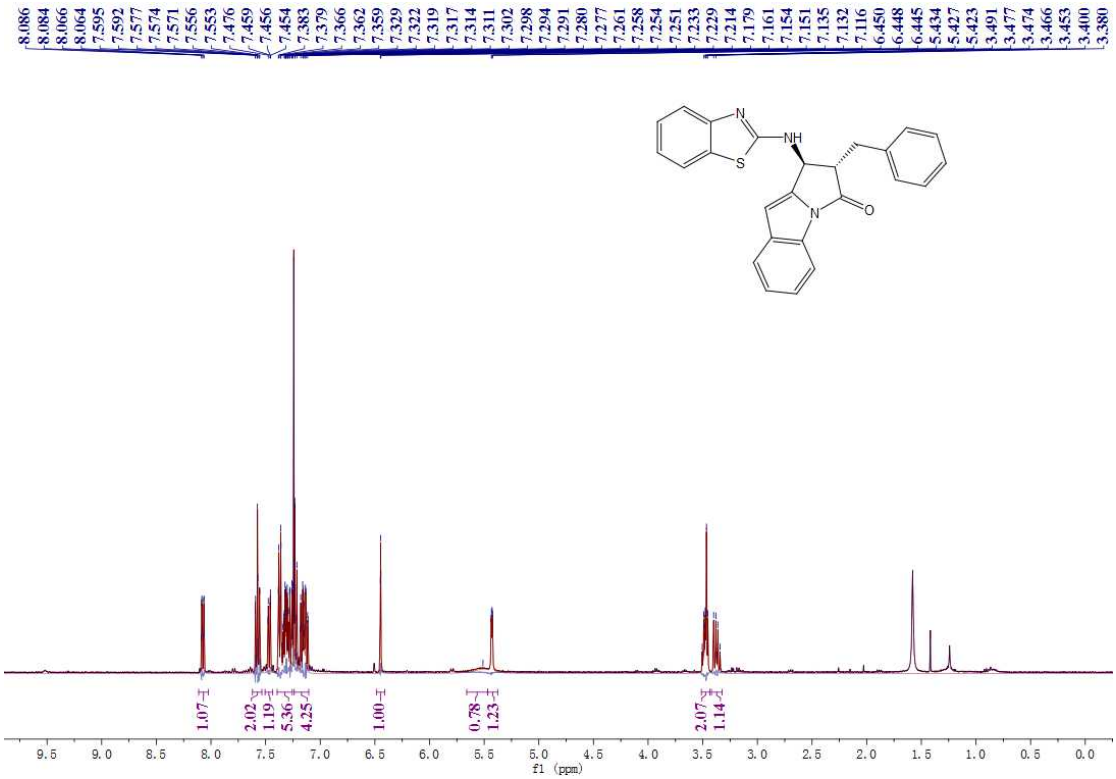
Name	Ni 87 a rac				
RT [min]	Type	Area%	Area	Height	Width [min]
4.18	BV	0.09	4.52	0.57	0.11
4.46	VV	0.88	43.69	6.36	0.10
4.71	VV	0.14	7.00	0.68	0.16
4.93	VV	0.14	6.95	0.79	0.13
5.17	VB	0.38	18.96	3.12	0.09
5.47	BB	0.20	9.94	0.60	0.22
7.72	VB	0.06	3.20	0.32	0.15
8.20	BB	0.04	2.09	0.21	0.15
8.99	BB	0.12	5.86	0.42	0.20
11.78	BB	0.08	4.03	0.20	0.27
21.26	BB	1.33	65.99	1.75	0.55
27.79	BB	47.87	2368.46	63.65	0.57
30.66	BB	1.01	49.79	1.22	0.62
39.60	BB	47.65	2357.54	41.39	0.88
	Sum	100.00	4948.02		

Enantioenriched **3m**

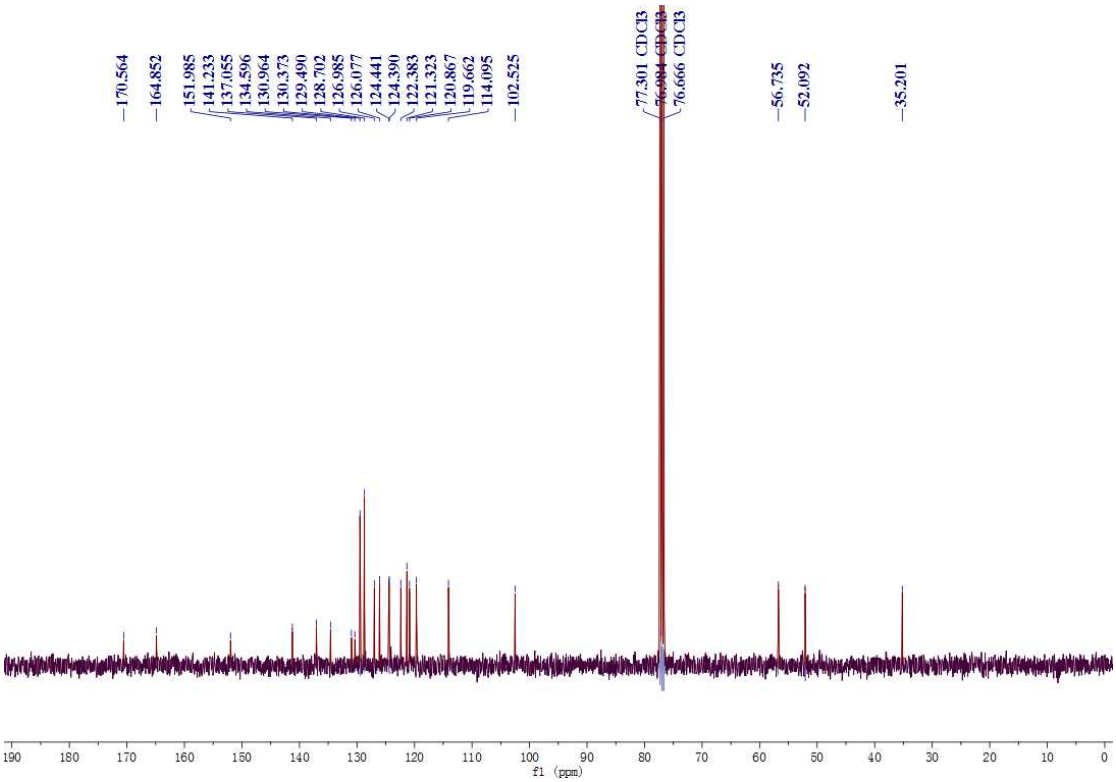


Name	Ni 87 b				
RT [min]	Type	Area%	Area	Height	Width [min]
4.47	VV	1.16	39.88	6.06	0.10
5.17	VB	0.55	19.09	3.22	0.09
14.42	BB	4.68	161.22	8.85	0.28
19.64	BB	0.59	20.25	0.64	0.45
27.73	BB	88.40	3043.43	82.43	0.57
30.60	BB	0.76	26.07	0.63	0.60
39.53	BB	3.86	132.91	2.20	0.86
	Sum	100.00	3442.85		

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



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



HPLC analysis: rac-**3n**

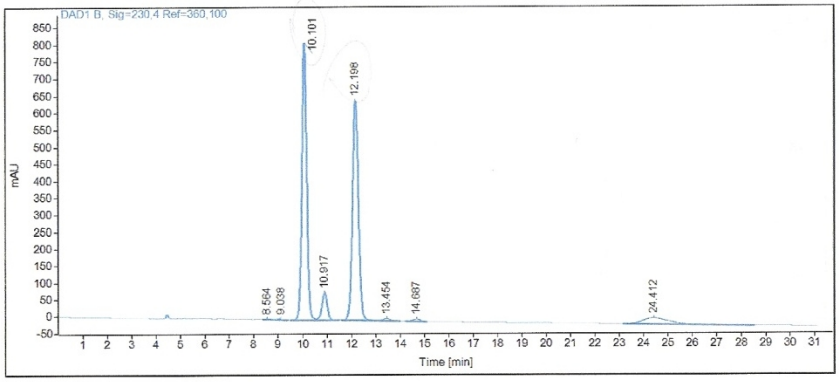
Sample name: **Ni 88 a rac**

Data file: C:\SNOOPY\NI\NI 88 A RAC IA.D
Description: Laufmittel: n-Heptan/EtOH 7:3 Die Probe ist DCM/LM gelöst.

Injection date: 9/15/2014 8:41:12 AM
Acq. Analysis method: CHIRALPAKIARNP.M

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

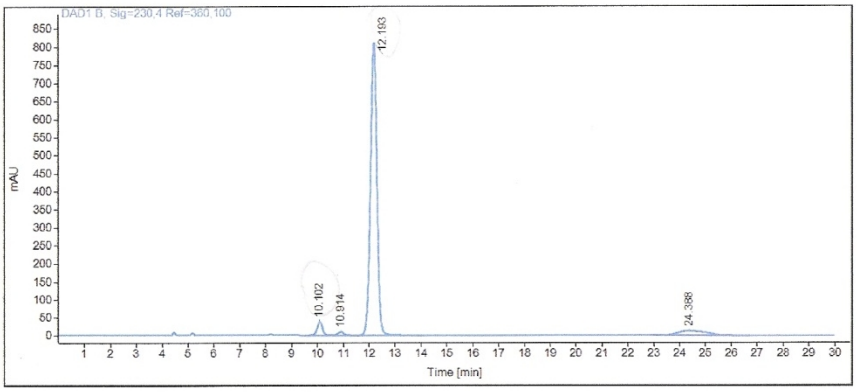
Pressure at start: 42 bar Start flow: 0.700 ml/min Column oven: 30 °C



Name Ni 88 a rac

RT [min]	Type	Area%	Area	Height	Width [min]
8.56	VB	0.09	22.65	1.33	0.27
9.04	BB	0.10	26.14	1.72	0.23
10.10	BV	44.33	11211.09	816.05	0.21
10.92	VB	4.92	1244.05	81.61	0.23
12.20	BV	44.23	11185.47	649.48	0.26
13.45	VB	0.55	138.39	7.10	0.30
14.69	BB	0.49	123.64	6.15	0.31
24.41	BBA	5.30	1339.96	18.36	1.08
	Sum	100.00	25291.39		

Enantioenriched **3n**



Name Ni 88 b

RT [min]	Type	Area%	Area	Height	Width [min]
10.10	BV	3.46	539.64	38.00	0.22
10.91	VV	0.92	143.88	9.17	0.24
12.19	VB	89.22	13913.40	810.27	0.26
24.39	BB	6.40	997.83	12.96	1.11
	Sum	100.00	15594.75		