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. Microanalyses were performed with a Vario EL element analyser. 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 [Daicel AD, Daicel AS, Daicel OD, Daicel OJ, Daicel (s,s)-Whelk O1 or Daicel Whelk.M].

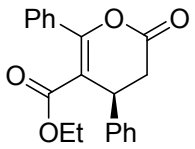
2. Materials

All reactions were carried out under argon. Toluene and mesitylene were distilled over Solvona®. Dry dichloromethane was purchased from Acros. All other chemicals were used without further purification. Triazolium salts **A-G** were prepared according to known literature procedures.[1] The corresponding α,β-unsaturated N-acyltriazoles **2** were prepared according to the literature.[2] Racemic samples were prepared with precatalyst **A**.

3. General procedure

To a dried and argon-filled Schlenk flask was added 1,3-dicarbonyl compound **1** (0.5 mmol, 1.0 equiv.), α,β-unsaturated N-acyltriazole **2** (1.0 mmol, 2.0 equiv.), triazolium salt **D** (0.1 mmol, 20 mol%) and 3 Å MS (100 mg) in toluene (5 mL). The mixture was cooled down to –5 °C and then K_2CO_3 (0.2 mmol, 40 mol%) was added. After stirring for 48 h at –5 °C, the solution was directly purified by flash chromatography on silica gel (*n*-pentane/Et_2O 4:1 or DCM) to afford the products **3a-o**.

4. Characterization Data



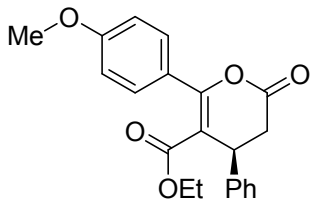
The compound **3a** was prepared according to the general procedure. The product was obtained as colorless oil (105.6 mg, 66% yield). The ee (86%) was measured by HPLC using a chiral stationary phase [Daicel AS, *n*-heptane:EtOH = 9:1, 1.0 mL/min), t_R = 11.13 min (major), 9.27 min (minor)], $[\alpha]_D^{21}$ = +70.7 (c = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 - 7.51 (m, 2H), 7.47 - 7.40 (m, 3H), 7.35 - 7.33 (m, 2H), 7.29 - 7.26 (m, 3H), 4.41 (dd, *J* = 7.7, 2.5 Hz, 1H), 3.98 - 3.89 (m, 2H), 3.11 (dd, *J* = 15.9, 7.7 Hz, 1H), 2.94 (dd, *J* = 15.9, 2.5 Hz, 1H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.35, 166.00, 158.52, 139.89, 133.08, 130.13, 129.19 (2C), 128.63 (2C), 127.99 (2C), 127.74, 126.74 (2C), 111.69, 61.00, 38.84, 36.31, 13.45 ppm.

MS (EI, 70 eV) m/z (%): 322 [M^+] (60), 294 (18), 279 (20), 248 (45), 220 (23), 105 (100), 77 (35).

IR (ATR): 2984, 2324, 2097, 1891, 1778, 1704, 1448, 1300, 1238, 1067, 846, 755, 698 cm^{-1}.

HRMS (EI): calcd for $C_{20}H_{18}O_4$ [M^+]: 322.1200; found: 322.1203.



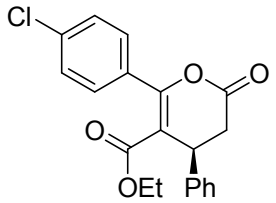
The compound **3b** was prepared according to the general procedure. The product was obtained as colorless oil (125.0 mg, 71% yield). The ee (82%) was measured by HPLC using a chiral stationary phase [Daicel AD, *n*-heptane:*i*-PrOH = 9:1, 1.0 mL/min), t_R = 13.48 min (major), 10.58 min (minor)], $[\alpha]_D^{21}$ = +46.0 (c = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 - 7.45 (m, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.29 - 7.22 (m, 3H), 6.95 - 6.89 (m, 2H), 4.39 (dd, *J* = 7.7, 2.5 Hz, 1H), 4.02 - 3.93 (m, 2H), 3.85 (s, 3H), 3.08 (dd, *J* = 15.8, 7.6 Hz, 1H), 2.92 (dd, *J* = 15.9, 2.5 Hz, 1H), 0.95 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.63, 166.24, 161.12, 158.29, 140.05, 130.34 (2C), 129.14 (2C), 127.66, 126.74 (2C), 125.15, 113.32 (2C), 110.60, 60.96, 55.37, 38.97, 36.39, 13.65 ppm.

MS (EI, 70 eV) m/z (%): 352 [M^+] (72), 278 (14), 135 (100), 77 (22).

IR (ATR): 2969, 2315, 2095, 1901, 1775, 1703, 1610, 1507, 1242, 1059, 840, 767, 702, 541 cm^{-1}.

HRMS (ESI): calcd for $C_{21}H_{20}O_5$ [M+Na]$^+$: 375,1203; found: 375.1201.



The compound **3c** was prepared according to the general procedure. The product was obtained as light yellow oil (168.1 mg, 94% yield). The ee (76%) was measured by HPLC using a chiral

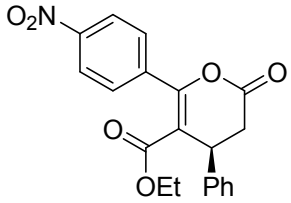
stationary phase [Daicel AD, *n*-heptane:*i*-PrOH = 9:1, 1.0 mL/min), t_R = 9.43 min (major), 7.73 min (minor)], $[\alpha]_D^{21}$ = +63.0 (c = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 - 7.44 (m, 2H), 7.41 - 7.38 (m, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.30 - 7.26 (m, 1H), 7.23 (d, *J* = 7.4 Hz, 2H), 4.40 (dd, *J* = 7.7, 2.5 Hz, 1H), 4.00 - 3.91 (m, 2H), 3.09 (dd, *J* = 15.9, 7.7 Hz, 1H), 2.94 (dd, *J* = 16.0, 2.5 Hz, 1H), 0.93 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.96, 165.70, 157.38, 139.69, 136.25, 131.43, 130.08 (2C), 129.23 (2C), 128.27 (2C), 127.82, 126.68 (2C), 112.10, 61.16, 38.85, 36.19, 13.55 ppm.

MS (EI, 70 eV) m/z (%): 356 [M^+] (74), 313 (27), 282 (40), 254 (24), 139 (100), 111 (31).

IR (ATR): 2982, 2320, 2092, 1910, 1781, 1706, 1486, 1299, 1241, 1070, 991, 845, 753, 698 cm^{-1}.

HRMS (EI): calcd for $C_{20}H_{17}ClO_4$ [$M]^+$: 356.0810; found: 356.0812.



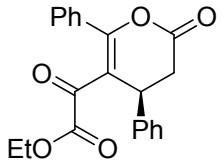
The compound **3d** was prepared according to the general procedure. The product was obtained as yellow oil (176.2 mg, 96% yield). The ee (62%) was measured by HPLC using a chiral stationary phase [Daicel (s,s)-Whelk O1, *n*-heptane:EtOH = 7:3, 0.5 mL/min), t_R = 17.08 min (major), 14.00 min (minor)], $[\alpha]_D^{21}$ = +70.8 (c = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 - 8.25 (m, 2H), 7.71 - 7.67 (m, 2H), 7.37 - 7.33 (m, 2H), 7.31 - 7.27 (m, 1H), 7.26 - 7.22 (m, 2H), 4.44 (dd, *J* = 7.7, 2.6 Hz, 1H), 3.96 (q, *J* = 7.1 Hz, 2H), 3.14 (dd, *J* = 16.0, 7.7 Hz, 1H), 2.98 (dd, *J* = 16.0, 2.6 Hz, 1H), 0.92 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.22, 165.07, 156.27, 148.51, 139.37, 139.20, 129.89 (2C), 129.33 (2C), 127.99, 126.63 (2C), 123.21 (2C), 113.61, 61.40, 38.82, 36.00, 13.55 ppm.

MS (EI, 70 eV) m/z (%): 367 [M^+] (55), 324 (42), 293 (51), 265 (30), 150 (90), 104 (100), 92 (46), 76 (84).

IR (ATR): 2986, 2321, 2095, 1923, 1784, 1708, 1600, 1518, 1342, 1244, 1074, 989, 856, 749, 698 cm^{-1}.

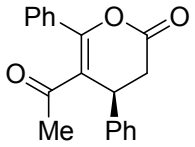
HRMS (EI): calcd for $C_{20}H_{17}NO_6$ [$M]^+$: 367.1050; found: 367.1051.



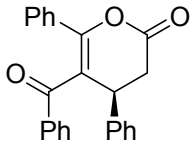
The compound **3e** was prepared according to the general procedure. The product was obtained as light yellow oil (153.3 mg, 77% yield). The ee (79%) was measured by HPLC using a chiral stationary phase [Daicel AD, *n*-heptane:*i*-PrOH = 7:3, 0.7 mL/min), t_R = 14.19 min (major), 9.95 min (minor)], $[\alpha]_D^{21}$ = +81.0 (c = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 - 7.65 (m, 2H), 7.51 - 7.47 (m, 1H), 7.36 - 7.32 (m, 2H), 7.28 - 7.21 (m, 3H), 7.15 - 7.11 (m, 2H), 4.17 (dd, *J* = 7.7, 3.1 Hz, 1H), 4.09 - 4.02 (m, 1H), 4.01 - 3.95 (m, 1H), 3.17 (dd, *J* = 16.2, 7.7 Hz, 1H), 3.03 (dd, *J* = 16.2, 3.1 Hz, 1H), 1.01 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.97, 164.91, 159.66, 140.29, 137.38, 136.11, 133.55, 129.33 (2C), 128.67 (2C), 128.60 (2C), 128.35, 128.18, 127.10 (2C), 62.48, 41.18, 35.15, 13.49

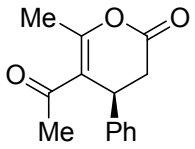
ppm.
MS (EI, 70 eV) m/z (%): 350 [M^+] (20), 277 (51), 235 (40), 105 (100), 77 (51).
IR (ATR): 2923, 2661, 2324, 2167, 2089, 1984, 1910, 1783, 1733, 1664, 1594, 1495, 1450, 1371, 1307, 1275, 1163, 1126, 1014, 957, 913, 856, 762, 698 cm^{-1}.
HRMS (ESI): calcd for $C_{21}H_{18}O_5$ [M+Na]$^+$: 373.1046; found: 373.1041.



The compound **3f** was prepared according to the general procedure. The product was obtained as colorless oil (109.5 mg, 75% yield). The ee (81%) was measured by HPLC using a chiral stationary phase [Daicel OJ, *n*-heptane:EtOH = 8:2, 1.0 mL/min), t_R = 23.61 min (major), 17.37 min (minor)], $[\alpha]_D^{21}$ = +62.0 (c = 1.0, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 - 7.61 (m, 2H), 7.53 - 7.50 (m, 1H), 7.41 - 7.37 (m, 2H), 7.28 - 7.24 (m, 2H), 7.23 - 7.18 (m, 1H), 7.16 - 7.12 (m, 2H), 4.32 (dd, *J* = 7.3, 2.9 Hz, 1H), 3.06 (dd, *J* = 16.0, 7.6 Hz, 1H), 2.93 (dd, *J* = 16.0, 3.6 Hz, 1H), 1.90 (d, *J* = 1.1 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.77, 166.49, 154.73, 139.95, 138.40, 133.06, 129.13 (2C), 128.78 (2C), 128.71 (2C), 127.62, 126.75 (2C), 117.74, 39.41, 36.19, 19.01 ppm.
MS (EI, 70 eV) m/z (%): 293 [M^+] (60), 274 (19), 264 (56), 249 (18), 221 (30), 207 (21), 173 (51), 105 (100), 77 (48).
IR (ATR): 3028, 2099, 1777, 1641, 1598, 1493, 1446, 1384, 1315, 1224, 1175, 1116, 1032, 986, 899, 856, 805, 755, 698 cm^{-1}.
HRMS (EI): calcd for $C_{19}H_{16}O_3$ [M]$^+$: 292.1094; found: 292.1103.



The compound **3g** was prepared according to the general procedure. The product was obtained as a colorless solid (95.0 mg, 65% yield). The ee (82%) was measured by HPLC using a chiral stationary phase [Daicel Whelk.M, *n*-heptane:EtOH = 7:3, 0.7 mL/min), t_R = 14.19 min (major), 8.34 min (minor)], $[\alpha]_D^{21}$ = +14.8 (c = 1.0, $CHCl_3$). Melting point: 120 - 123 ^{o}C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 - 7.47 (m, 2H), 7.39 - 7.35 (m, 2H), 7.32 - 7.25 (m, 4H), 7.25 - 7.19 (m, 2H), 7.19 - 7.14 (m, 1H), 7.14 - 7.05 (m, 4H), 4.56 (dd, *J* = 7.9, 2.4 Hz, 1H), 3.21 (dd, *J* = 15.9, 7.9 Hz, 1H), 3.06 (dd, *J* = 15.9, 2.4 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.90, 166.67, 154.81, 139.70, 137.07, 132.59, 131.96, 130.29, 129.24 (2C), 129.22 (2C), 128.98 (2C), 128.05 (2C), 127.99 (2C), 127.78, 126.84 (2C), 118.27, 40.38, 35.95 ppm.
MS (EI, 70 eV) m/z (%): 354 [M^+] (9), 105 (100), 77 (92).
IR (ATR): 3061, 3030, 2105, 1778, 1640, 1493, 1448, 1411, 1323, 1249, 1187, 1113, 1025, 987, 900, 843, 757, 730, 696 cm^{-1}.
HRMS (EI): calcd for $C_{24}H_{18}O_3$ [M]$^+$: 354.1251; found: 354.1251.



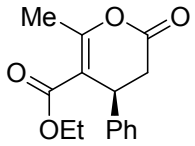
The compound **3h** was prepared according to the general procedure. The product was obtained as a colorless solid (78.5 mg, 68% yield). The ee (80%) was measured by HPLC using a chiral stationary phase [Daicel (s,s)-Whelk O1, *n*-heptane:EtOH = 9:1, 1.0 mL/min), t_R = 11.63 min (major), 9.93 min (minor)], $[\alpha]_D^{21}$ = +36.6 (c = 1.0, $CHCl_3$). Melting point: 68 - 69 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 - 7.30 (m, 2H), 7.28 - 7.24 (m, 1H), 7.15 - 7.11 (m, 2H), 4.17 - 4.11 (m, 1H), 2.95 (dd, *J* = 15.7, 7.3 Hz, 1H), 2.82 (dd, *J* = 15.7, 2.6 Hz, 1H), 2.41 (d, *J* = 1.1 Hz, 3H), 2.11 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.88, 165.59, 160.24, 139.69, 129.42 (2C), 127.92, 126.64 (2C), 117.26, 38.83, 37.16, 29.76, 19.07 ppm.

MS (EI, 70 eV) m/z (%): 230 [M^+] (35), 212 (42), 202 (48), 187 (76), 145 (57), 131 (100), 115 (55), 103 (58), 91 (31), 77 (70), 51 (59).

IR (ATR): 2920, 2089, 1781, 1688, 1609, 1492, 1450, 1423, 1359, 1291, 1268, 1242, 1172, 1114, 1025, 943, 863, 770, 702, 660 cm^{-1}.

Anal. calcd. for $C_{14}H_{14}O_3$ (230) C, 73.03; H, 6.13; found: C, 72.93; H, 6.04.



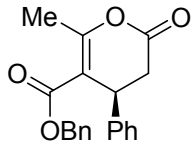
The compound **3i** was prepared according to the general procedure. The product was obtained as a colorless solid (105.3 mg, 81% yield). The ee (85%) was measured by HPLC using a chiral stationary phase [Daicel (s,s)-Whelk O1, *n*-heptane:EtOH = 7:3, 0.7 mL/min), t_R = 6.80 min (major), 5.79 min (minor)], $[\alpha]_D^{21}$ = +202.0 (c = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 - 7.28 (m, 2H), 7.25 - 7.22 (m, 1H), 7.15 - 7.12 (m, 2H), 4.27 - 4.24 (m, 1H), 4.15 - 4.12 (m, 2H), 2.95 (dd, *J* = 15.9, 7.6 Hz, 1H), 2.83 (dd, *J* = 15.9, 2.2 Hz, 1H), 2.47 (d, *J* = 1.0 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.13, 165.93, 161.31, 140.60, 129.01 (2C), 127.48, 126.58 (2C), 109.99, 60.85, 37.82, 36.36, 18.88, 14.05 ppm.

MS (EI, 70 eV) m/z (%): 260 [M^+] (40), 217 (32), 186 (48), 171 (23), 158 (90), 144 (24), 131 (75), 115 (93), 103 (85), 91 (47), 77 (100).

IR (ATR): 2987, 2280, 2213, 2126, 2084, 2017, 1775, 1710, 1644, 1494, 1452, 1369, 1281, 1242, 1175, 1122, 1066, 972, 864, 764, 705, 668 cm^{-1}.

HRMS (EI): calcd for $C_{15}H_{16}O_4$ [$M]^+$: 260.1046; found: 260.1043.



The compound **3j** was prepared according to the general procedure. The product was obtained as a colorless solid (100.0 mg, 62% yield). The ee (83%) was measured by HPLC using a chiral stationary phase [Daicel (s,s)-Whelk O1, *n*-heptane:EtOH = 7:3, 0.7 mL/min), t_R = 7.80 min

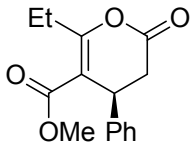
(major), 6.58 min (minor)], $[\alpha]_D^{21}$ = +55.8 (c = 1.0, $CHCl_3$). Melting point: 92 - 95 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 - 7.20 (m, 6H), 7.15 - 7.02 (m, 4H), 5.14 - 5.04 (m, 2H), 4.26 (d, *J* = 7.3 Hz, 1H), 2.93 (dd, *J* = 15.8, 7.6 Hz, 1H), 2.80 (dd, *J* = 15.8, 2.2 Hz, 1H), 2.47 (d, *J* = 1.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.89, 165.66, 162.02, 140.50, 135.55, 129.05 (2C), 128.45 (2C), 128.13, 127.85 (2C), 127.53, 126.62 (2C), 109.58, 66.54, 37.87, 36.36, 18.93 ppm.

MS (EI, 70 eV) m/z (%): 322 [M^+] (1), 231 (19), 91 (100).

IR (ATR): 3063, 3028, 2320, 2204, 2083, 2010, 1901, 1778, 1710, 1638, 1492, 1449, 1379, 1285, 1228, 1177, 1114, 1065, 864, 798, 701 cm^{-1}.

Anal. calcd. for $C_{20}H_{18}O_4$ (322) C, 74.52; H, 5.63; found: C, 74.39; H, 5.65.



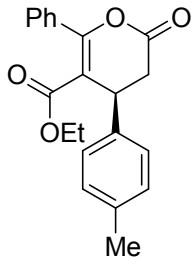
The compound **3k** was prepared according to the general procedure. The product was obtained as colorless oil (114.4 mg, 88% yield). The ee (83%) was measured by HPLC using a chiral stationary phase [Daicel (s,s)-Whelk O1, *n*-heptane:EtOH = 9:1, 1.0 mL/min), t_R = 6.78 min (major), 5.68 min (minor)], $[\alpha]_D^{21}$ = +152.0 (c = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 - 7.27 (m, 2H), 7.26 - 7.21 (m, 1H), 7.14 - 7.09 (m, 2H), 4.25 (dd, *J* = 7.7, 2.1 Hz, 1H), 3.67 (d, *J* = 1.3 Hz, 3H), 2.96 - 2.87 (m, 2H), 2.87 - 2.78 (m, 2H), 1.27 (td, *J* = 7.5, 0.8 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.36, 166.23, 166.19, 140.34, 129.07 (2C), 127.52, 126.51 (2C), 108.94, 51.91, 37.70, 36.52, 25.47, 11.78 ppm.

MS (EI, 70 eV) m/z (%): 260 [M^+] (66), 228 (53), 217 (19), 203 (40), 200 (73), 189 (100), 172 (29), 157 (20), 131 (23), 121 (70), 115 (29), 57 (24).

IR (ATR): 3025, 2109, 1782, 1711, 1643, 1436, 1352, 1282, 1215, 1171, 1114, 1052, 975, 941, 866, 751, 701, 666 cm^{-1}.

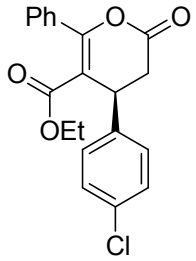
HRMS (EI): calcd for $C_{15}H_{16}O_4$ $[M]^+$: 260.1043; found: 260.1050.



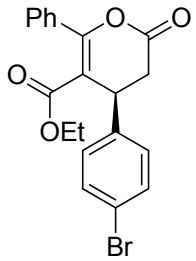
The compound **3l** was prepared according to the general procedure. The product was obtained as a white solid (109.2 mg, 65% yield). The ee (77%) was measured by HPLC using a chiral stationary phase [Daicel OD, *n*-heptane:*i*-PrOH = 9:1, 0.7 mL/min), t_R = 11.10 min (major), 12.78 min (minor)], $[\alpha]_D^{21}$ = +65.4 (c = 1.0, $CHCl_3$). Melting point: 92 - 94 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 - 7.49 (m, 2H), 7.47 - 7.38 (m, 3H), 7.14 (s, 4H), 4.37 (dd, *J* = 7.7, 2.4 Hz, 1H), 3.98 - 3.89 (m, 2H), 3.08 (dd, *J* = 15.8, 7.7 Hz, 1H), 2.92 (dd, *J* = 15.8, 2.4 Hz, 1H), 2.32 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.40, 166.10, 158.31, 137.40, 136.84, 133.14, 130.06, 129.84 (2C), 128.62 (2C), 127.95 (2C), 126.60 (2C),

111.91, 60.96, 38.48, 36.41, 21.04, 13.45 ppm.
MS (EI, 70 eV) m/z (%): 336 [M^+] (46), 279 (18), 262 (32), 234 (20), 105 (100), 77 (59).
IR (ATR): 3921, 3784, 3472, 2983, 2654, 2319, 2079, 1993, 1912, 1784, 1708, 1645, 1512, 1449, 1368, 1303, 1233, 1187, 1112, 1069, 988, 853, 769, 698 cm^{-1}.
Anal. calcd. for $C_{21}H_{20}O_4$ (336) C, 74.98; H, 5.99; found: C, 74.82; H, 6.03.

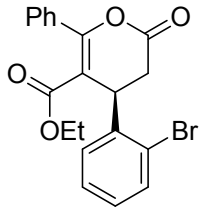


The compound **3m** was prepared according to the general procedure. The product was obtained as a colorless solid (119.5 mg, 67% yield). The ee (79%) was measured by HPLC using a chiral stationary phase [Daicel AD, *n*-heptane:*i*-PrOH = 9:1, 1.0 mL/min), t_R = 11.94 min (major), 8.66 min (minor)], $[\alpha]_D^{21}$ = +55.0 (c = 1.0, $CHCl_3$). Melting point: 69 - 71 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 - 7.48 (m, 2H), 7.48 - 7.44 (m, 1H), 7.44 - 7.39 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 4.38 (dd, *J* = 7.8, 2.3 Hz, 1H), 4.00 - 3.89 (m, 2H), 3.10 (dd, *J* = 15.9, 7.7 Hz, 1H), 2.91 (dd, *J* = 15.9, 2.3 Hz, 1H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.20, 165.64, 158.87, 138.41, 133.63, 132.86, 130.27, 129.38 (2C), 128.61 (2C), 128.15 (2C), 128.01 (2C), 111.23, 61.11, 38.29, 36.14, 13.45 ppm.
MS (EI, 70 eV) m/z (%): 356 [M^+] (29), 282 (28), 105 (100), 77 (51).
IR (ATR): 3386, 2982, 2660, 2324, 2112, 1908, 1781, 1702, 1644, 1490, 1445, 1409, 1371, 1341, 1303, 1238, 1183, 1109, 1066, 989, 849, 765, 729, 696 cm^{-1}.
HRMS (EI): calcd for $C_{20}H_{17}ClO_4$ [$M]^+$: 356.0810; found: 356.0813.



The compound **3n** was prepared according to the general procedure. The product was obtained as a colorless solid (150.2 mg, 78% yield). The ee (76%) was measured by HPLC using a chiral stationary phase [Daicel AD, *n*-heptane:*i*-PrOH = 9:1, 1.0 mL/min), t_R = 12.83 min (major), 9.23 min (minor)], $[\alpha]_D^{21}$ = +47.5 (c = 1.0, $CHCl_3$). Melting point: 91 - 93 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 - 7.48 (m, 2H), 7.48 - 7.43 (m, 3H), 7.43 - 7.38 (m, 2H), 7.16 - 7.11 (m, 2H), 4.37 (dd, *J* = 7.7, 2.4 Hz, 1H), 3.99 - 3.89 (m, 2H), 3.10 (dd, *J* = 15.9, 7.8 Hz, 1H), 2.90 (dd, *J* = 15.9, 2.4 Hz, 1H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.16, 165.59, 158.90, 138.98, 132.88, 132.32 (2C), 130.27, 128.61 (2C), 128.51 (2C), 128.01 (2C), 121.71, 111.16, 61.10, 38.36, 36.05, 13.45 ppm.
MS (EI, 70 eV) m/z (%): 400 [M^+] (6), 105 (100), 77 (74).

IR (ATR): 2982, 2322, 2082, 1903, 1781, 1703, 1642, 1487, 1407, 1299, 1237, 1182, 1110, 1066, 993, 940, 843, 766, 696 cm^{-1}.
Anal. calcd. for $C_{20}H_{17}BrO_4$ (400) C, 59.87; H, 4.27; found: C, 59.81; H, 4.31.



The compound **3o** was prepared according to the general procedure. The product was obtained as a colorless solid (142.5 mg, 74% yield). The ee (79%) was measured by HPLC using a chiral stationary phase [Daicel OD, *n*-heptane:*i*-PrOH = 9:1, 1.0 mL/min), t_R = 12.16 min (major), 8.50 min (minor)], $[\alpha]_D^{21}$ = +216.0 (c = 1.0, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.58 - 7.54 (m, 2H), 7.50 - 7.41 (m, 3H), 7.29 (td, *J* = 7.5, 1.2 Hz, 1H), 7.22 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.15 (td, *J* = 7.6, 1.7 Hz, 1H), 4.91 (dd, *J* = 7.9, 2.4 Hz, 1H), 3.98 - 3.89 (m, 2H), 3.08 (dd, *J* = 16.0, 7.9 Hz, 1H), 2.99 (dd, *J* = 16.0, 2.3 Hz, 1H), 0.90 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.84, 165.50, 159.86, 138.15, 133.74, 132.76, 130.35, 129.42, 128.69 (2C), 128.30, 128.05 (2C), 127.28, 123.88, 110.66, 61.09, 38.42, 34.74, 13.49 ppm.
MS (EI, 70 eV) m/z (%): 400 [M^+] (2), 321 (46), 279 (71), 251 (22), 173 (18), 105 (100), 77 (74).
IR (ATR): 3061, 2983, 2164, 2067, 1784, 1706, 1645, 1464, 1370, 1343, 1300, 1238, 1186, 1119, 1066, 987, 944, 850, 760, 696 cm^{-1}.
HRMS (ESI): calcd for $C_{20}H_{17}BrO_4$ [M+Na]$^+$: 423.0202; found: 423.0202.

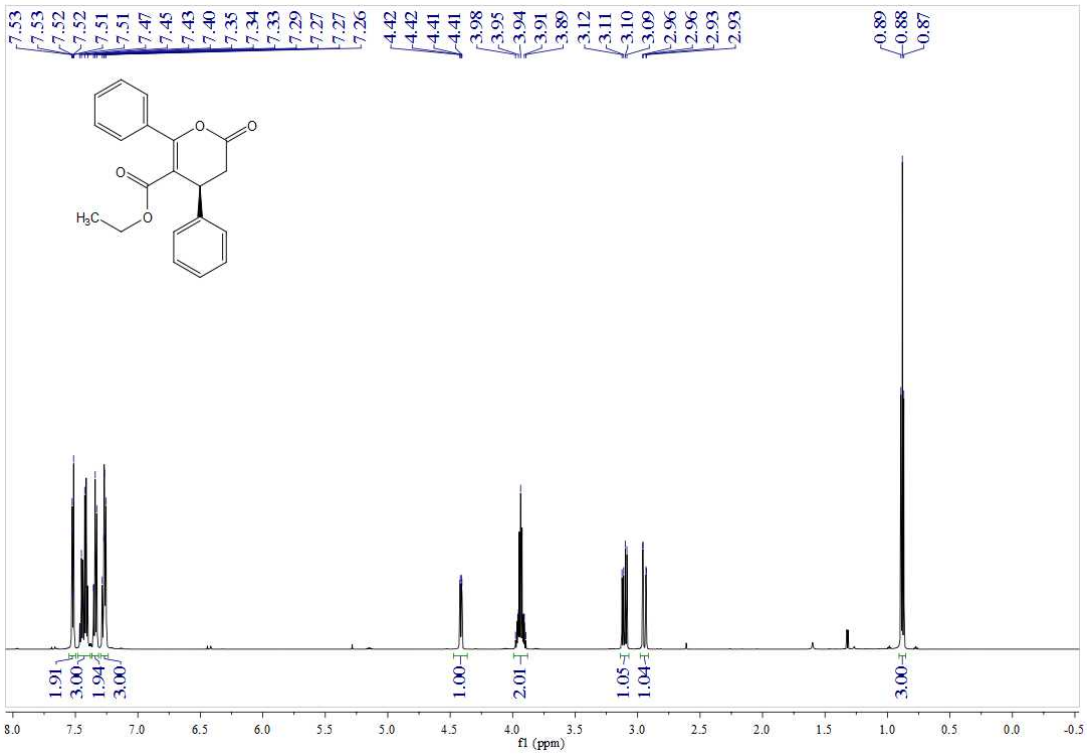
5. References

[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.

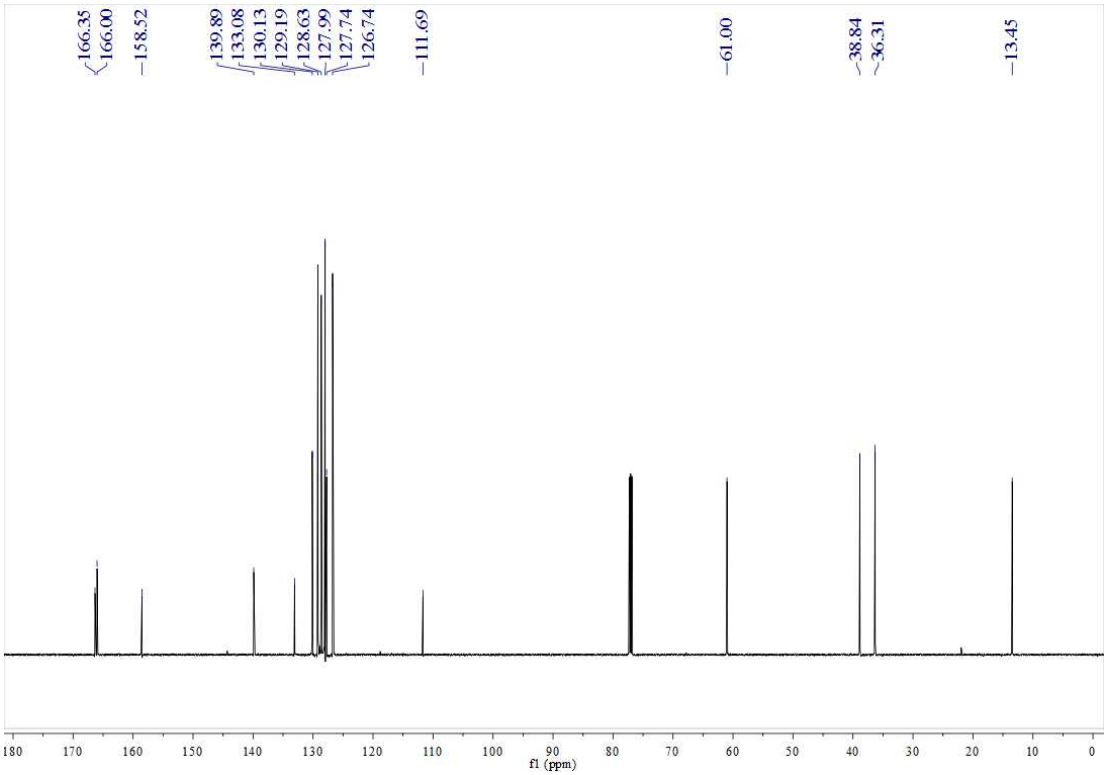
[2] G. Speranza , C. F. Morelli, P. Manitto, *Synthesis,* 2000, 123.

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

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

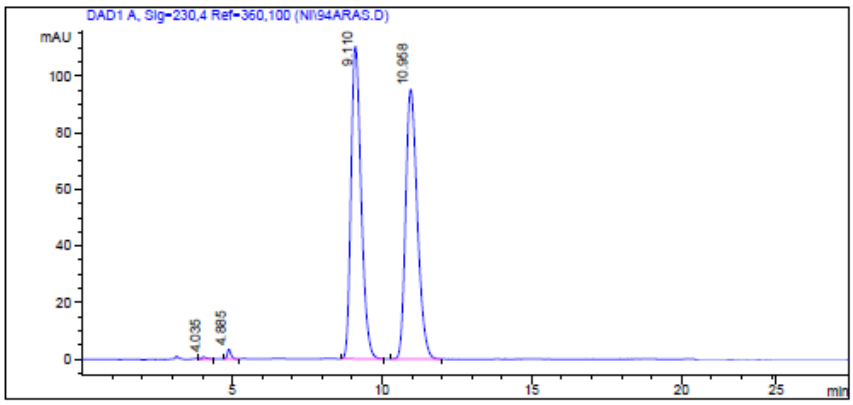


^{13}C NMR of **3a**



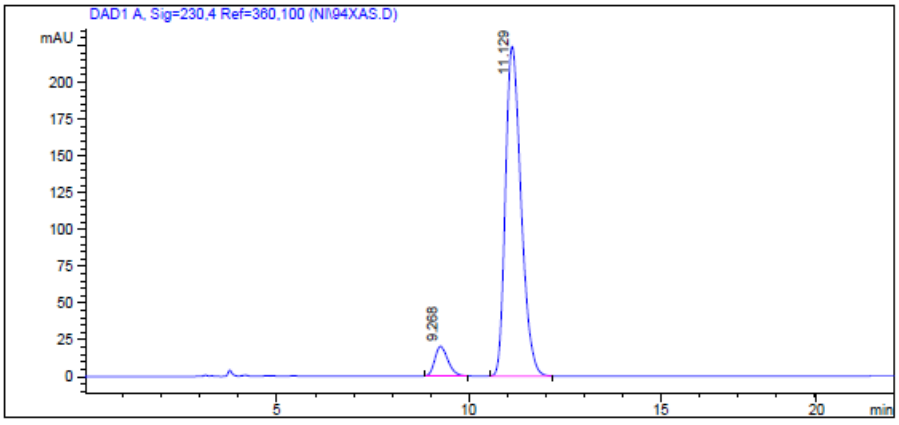
HPLC analysis: rac-**3a**

```
Data file:          D:\ERNIE\NI\94ARAS.D
Sample Info:        Laufmittel: n-Heptan/EtOH 9:1;
                    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:         10:25:40
Injektion Date:         08.01.2015

Instrument Conditions:    At Start              At Stop

Temperature in°C:         30.0                    30.0
Pressure in bar:          31.8                    32.0
Flow in ml/min:           1.0                     1.0
```



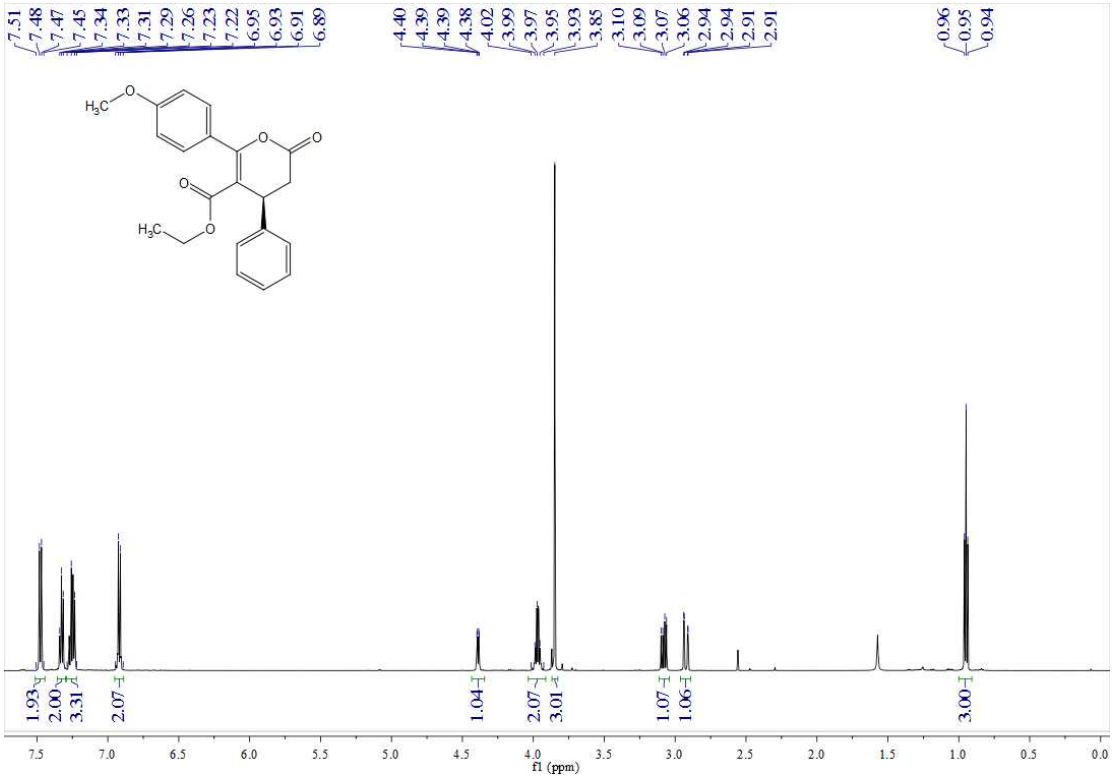
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.03	0.17	0.86	10.91	0.21
2	4.88	0.13	3.45	29.05	0.56
3	9.11	0.36	110.42	2580.36	49.60
4	10.96	0.42	95.22	2582.19	49.63
Total				5202.51	100.00

Enantioenriched **3a**

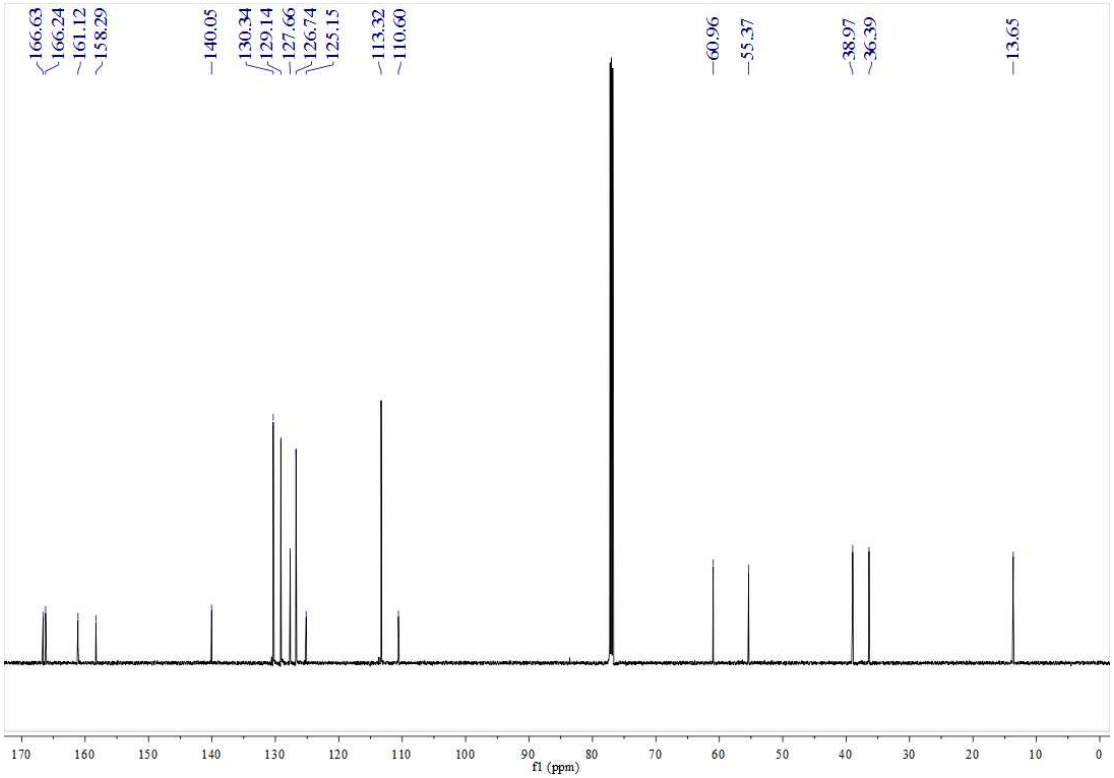


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	9.27	0.37	20.27	485.91	7.12
2	11.13	0.44	223.99	6334.98	92.88
Total				6820.89	100.00

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

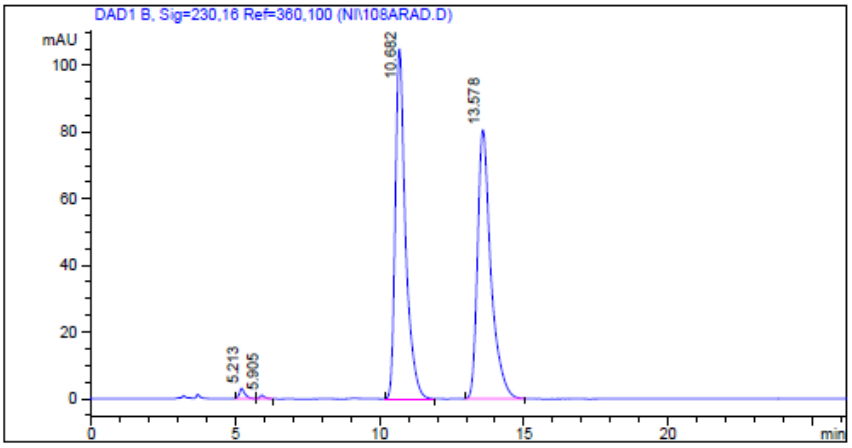


^{13}C NMR of **3b**



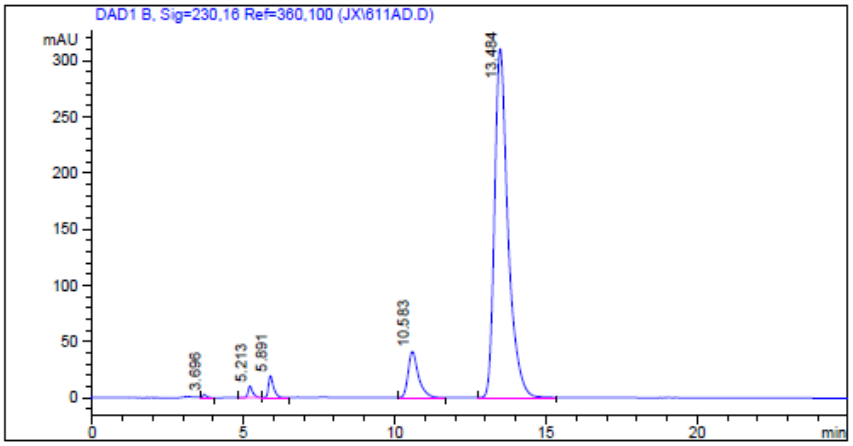
HPLC analysis: rac-**3b**

```
Data file:              D:\GONZO\NI\108ARAD.D
Sample Info:            Laufmittel: n-Heptan/iPrOH 9:1;
                        Die Probe ist in DCM/LM gelöst.

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

 Injektion Time:         14:17:30
 Injektion Date:         28.01.2015

 Instrument Conditions:   At Start              At Stop
 Temperature in°C:          30.0°C                30.0°C
 Pressure in bar:           31.9                  32.9
 Flow in ml/min:            1.00                  1.00
```



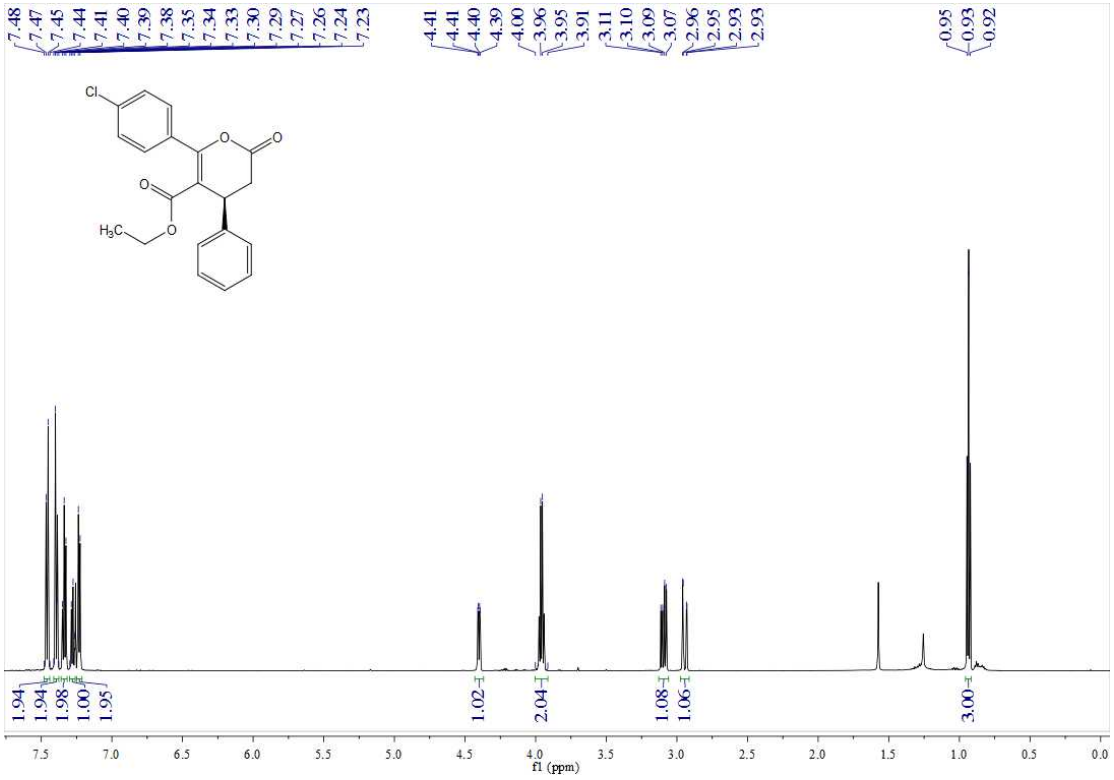
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.21	0.20	3.06	41.71	0.80
2	5.91	0.18	1.08	13.10	0.25
3	10.68	0.37	104.99	2593.82	49.49
4	13.58	0.48	80.71	2592.20	49.46
Total				5240.84	100.00

Enantioenriched **3b**

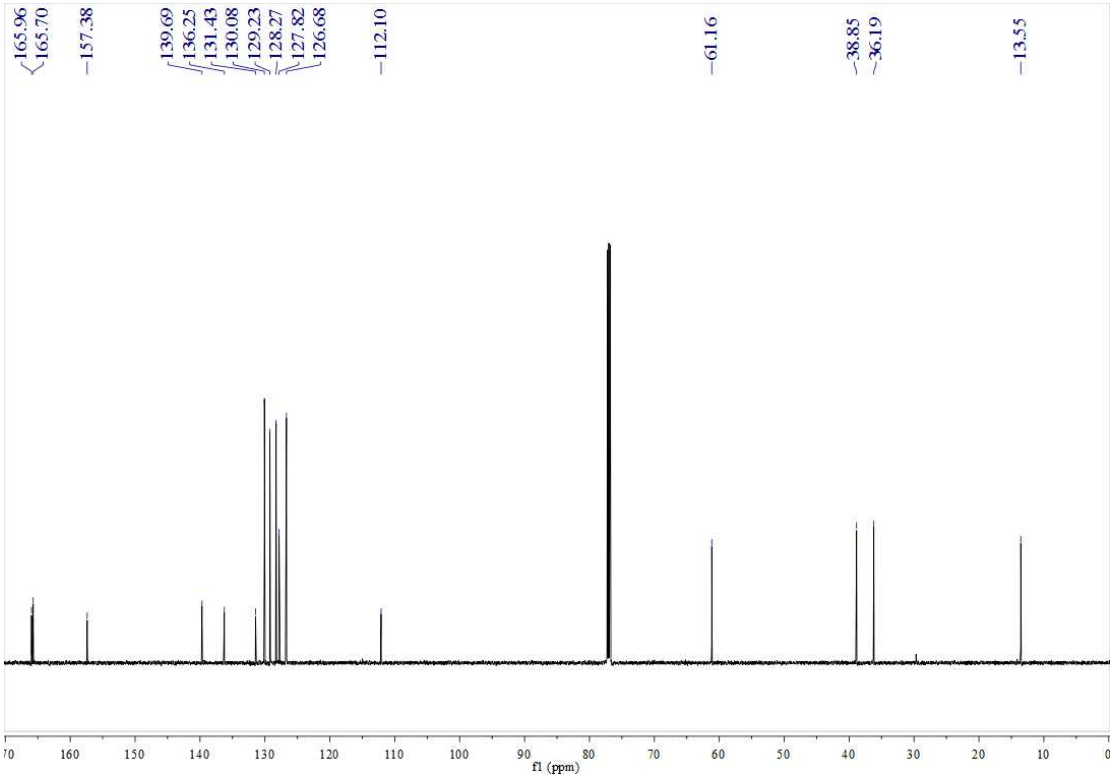


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.70	0.13	2.99	26.00	0.24
2	5.21	0.16	10.39	117.23	1.07
3	5.89	0.17	19.50	232.00	2.12
4	10.58	0.35	40.95	970.68	8.87
5	13.48	0.46	310.80	9603.18	87.71
Total				10949.09	100.00

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

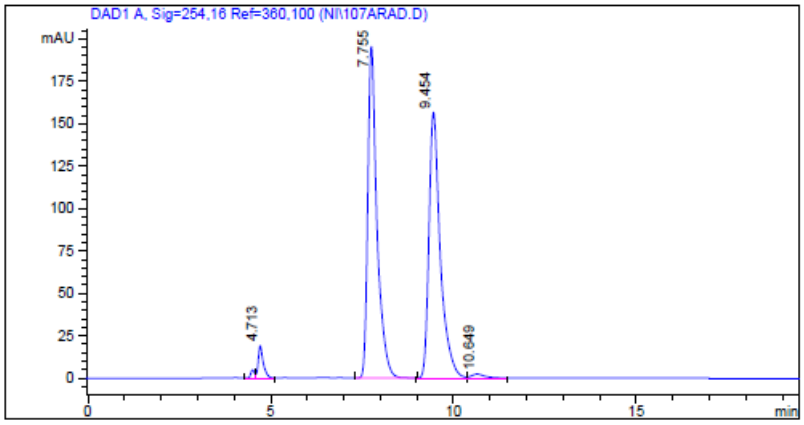


^{13}C NMR of **3c**



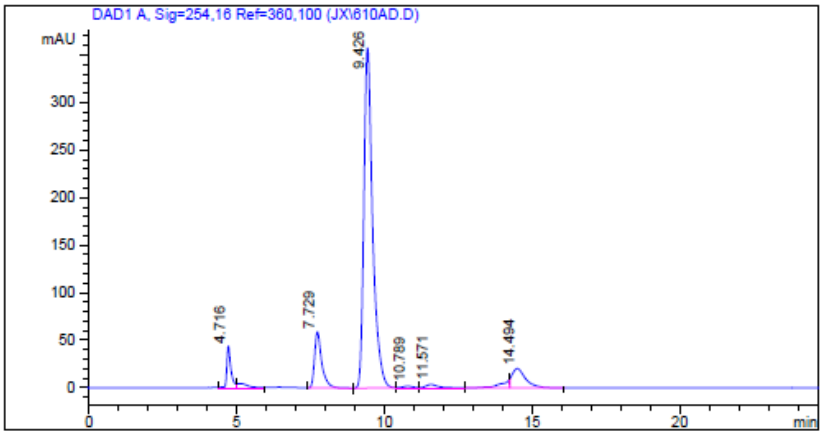
HPLC analysis: rac-**3c**

```
Data file:              D:\GONZO\NI\107ARAD.D
Sample Info:            Laufmittel: n-Heptan/iPrOH 9:1;
                        Die Probe ist in DCM/LM gelöst.

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

 Injektion Time:         13:54:24
 Injektion Date:         28.01.2015

 Instrument Conditions:   At Start              At Stop
 Temperature in°C:          30.0°C                30.0°C
 Pressure in bar:           32.0                  32.7
 Flow in ml/min:            1.00                  1.00
```



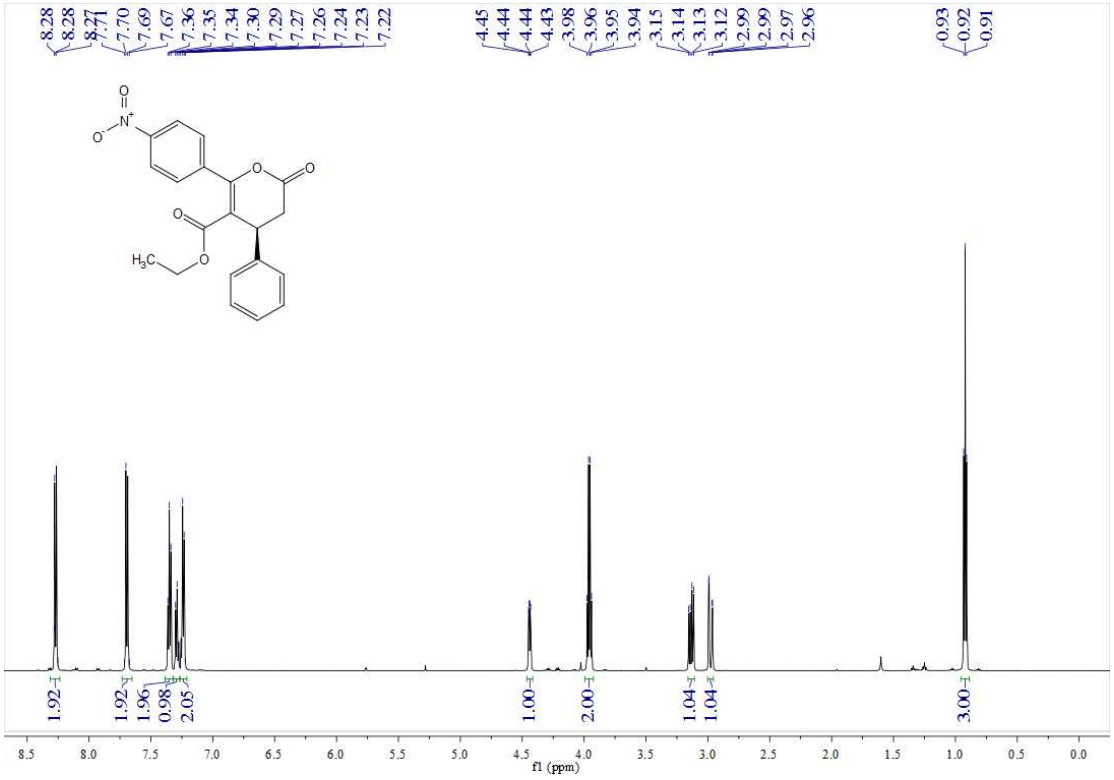
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.50	0.11	4.89	35.78	0.50
2	4.71	0.14	19.09	184.90	2.61
3	7.76	0.26	195.45	3427.11	48.36
4	9.45	0.32	156.58	3378.77	47.68
5	10.65	0.38	2.34	60.03	0.85
Total				7086.59	100.00

Enantioenriched **3c**

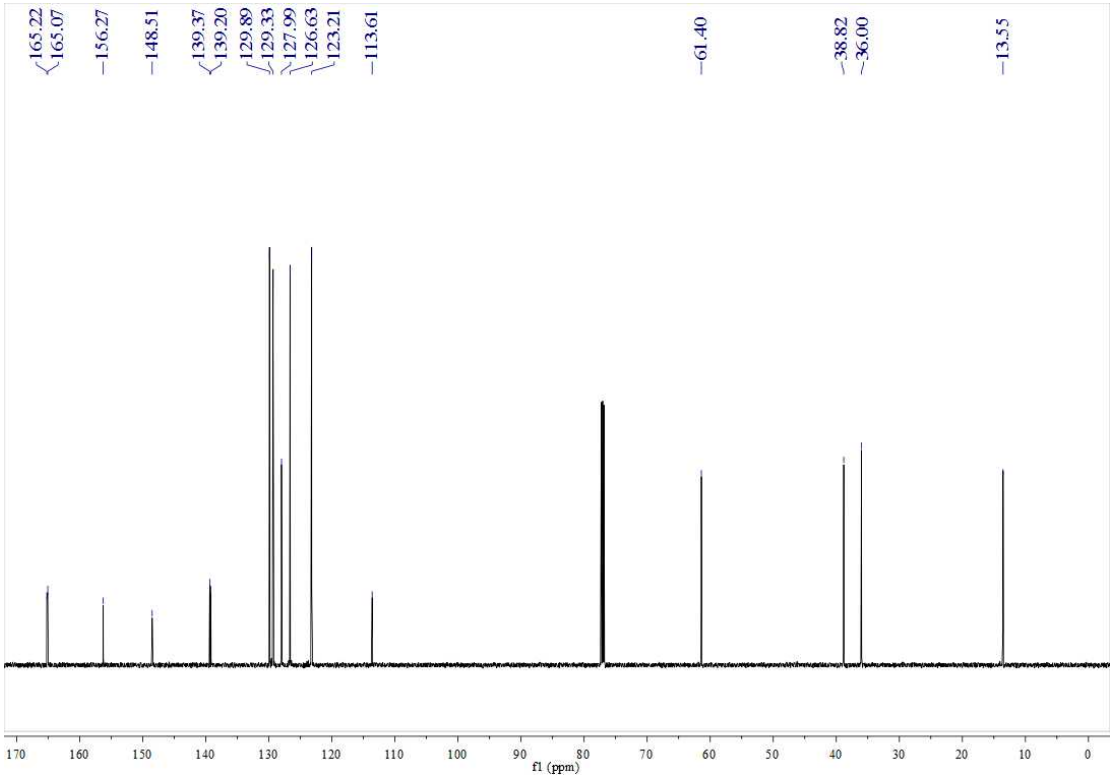


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.72	0.15	42.43	430.56	4.33
2	5.13	0.37	4.62	116.64	1.17
3	7.73	0.26	58.70	1009.51	10.16
4	9.43	0.31	357.26	7387.30	74.31
5	10.79	0.42	1.88	54.16	0.54
6	11.57	0.43	3.69	112.29	1.13
7	14.23	0.34	9.10	186.08	1.87
8	14.49	0.53	20.32	644.13	6.48
Total				9940.67	100.00

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



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



HPLC analysis: rac-**3d**

```
Data file:        D:\BERT\NI\103AR1W.D
Sample Info:      Laufmittel: n-Heptan/EtOH 7:3;
                  Die Probe ist in DCM/LM gelöst


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

Operator:         Analytik Labor AKEN

Injektion Time:       09:20:37
Injektion Date:       23.01.2015

Instrument Conditions:    At Start              At Stop

Temperature in°C:         30.0                    30.0
Pressure in bar:          32.1                    31.9
Flow in ml/min:           0.5                     0.5
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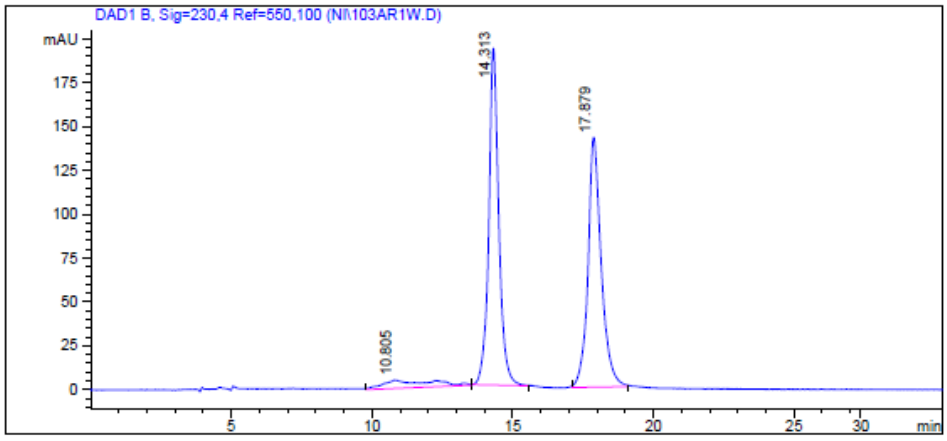
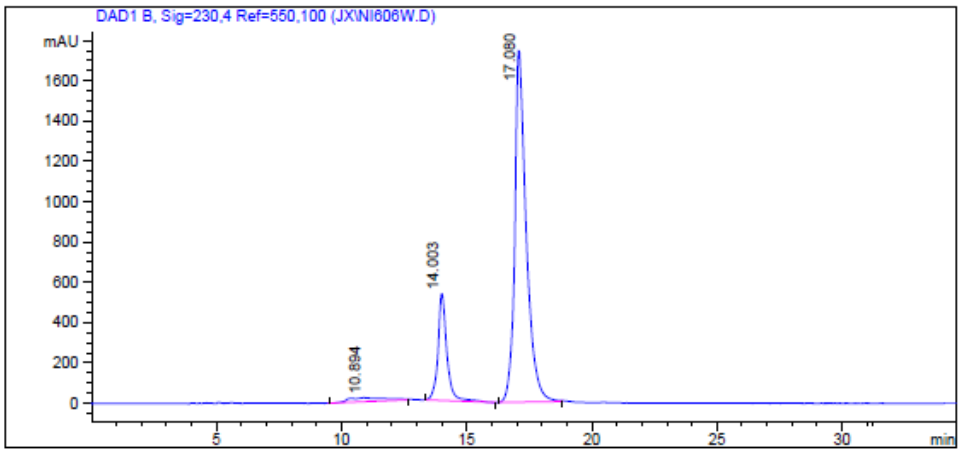


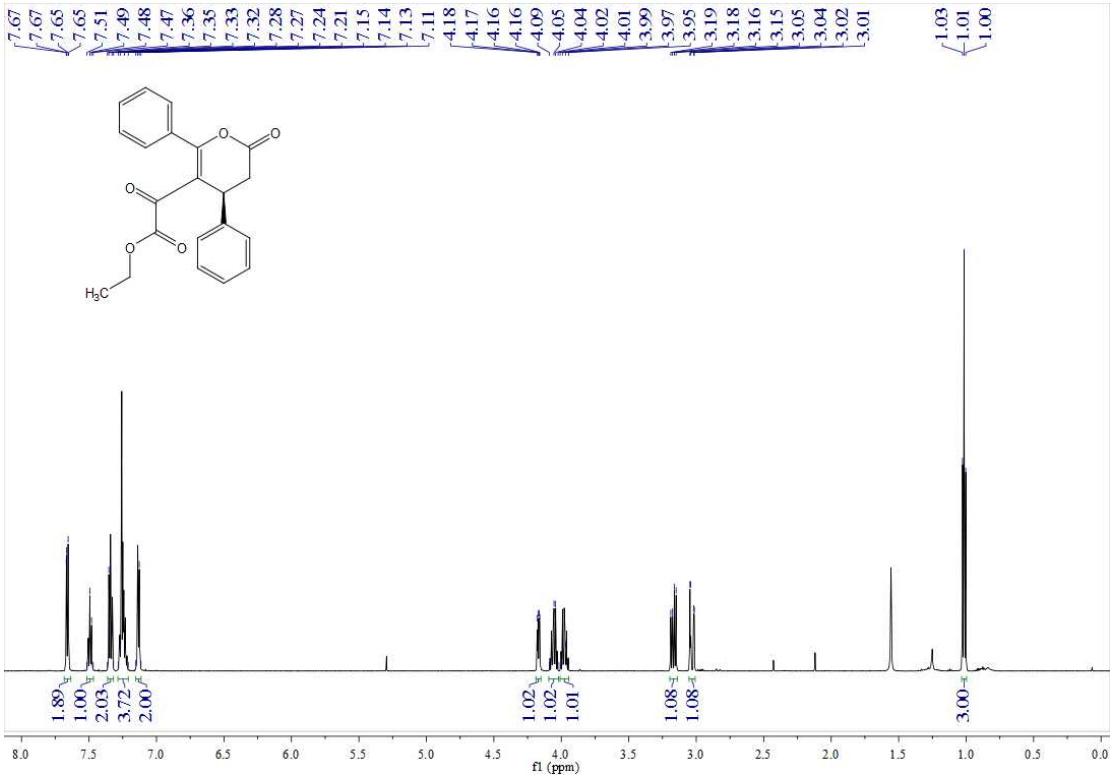
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	10.80	1.89	4.79	543.25	5.45
2	14.31	0.41	192.17	4771.17	47.86
3	17.88	0.47	142.52	4654.96	46.69
Total				9969.38	100.00

Enantioenriched **3d**

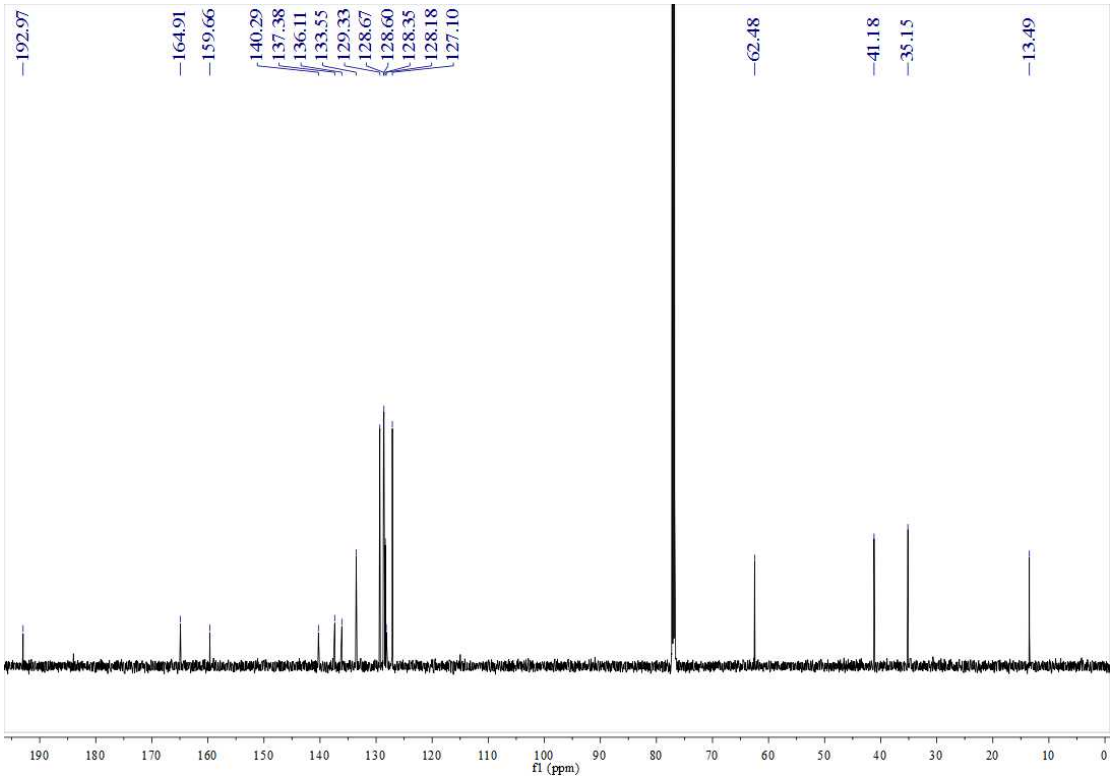


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	10.89	1.22	20.42	2074.81	2.92
2	14.00	0.36	530.83	13148.85	18.53
3	17.08	0.45	1743.92	55753.09	78.55
Total				70976.74	100.00

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



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



HPLC analysis: rac-**3e**

```
Data file:              D:\GONZO\NI\104AR1AD.D
Sample Info:            Laufmittel: n-Heptan/iPrOH 7:3;
                        Die Probe ist in DCM/LM gelöst.

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

 Injektion Time:         09:28:07
 Injektion Date:         26.01.2015

 Instrument Conditions:    At Start              At Stop
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 Pressure in bar:            28.1                  28.7
 Flow in ml/min:             0.70                  0.70
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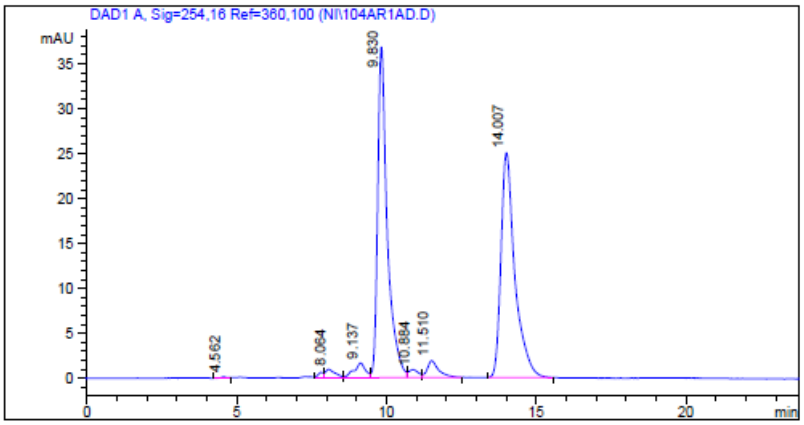
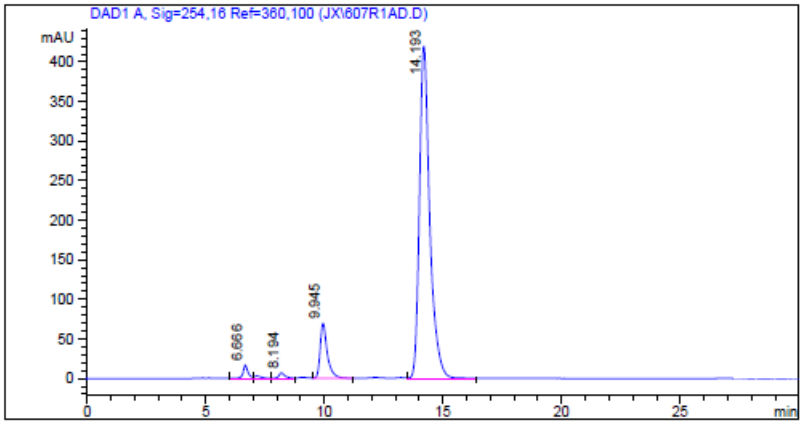


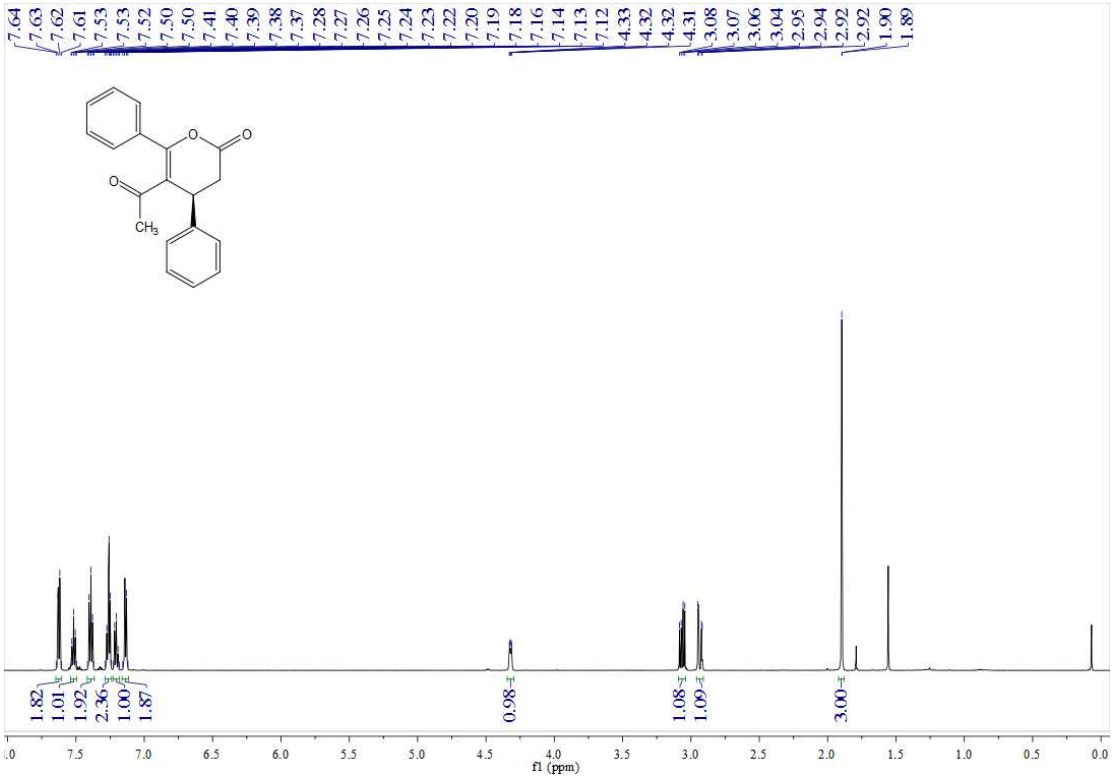
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.56	0.18	0.16	2.11	0.12
2	7.81	0.17	0.60	7.72	0.44
3	8.06	0.30	0.95	22.01	1.24
4	9.14	0.36	1.65	43.35	2.45
5	9.83	0.33	36.78	818.81	46.23
6	10.88	0.30	0.90	20.50	1.16
7	11.51	0.38	1.88	50.28	2.84
8	14.01	0.47	25.02	806.27	45.53
Total				1771.05	100.00

Enantioenriched **3e**

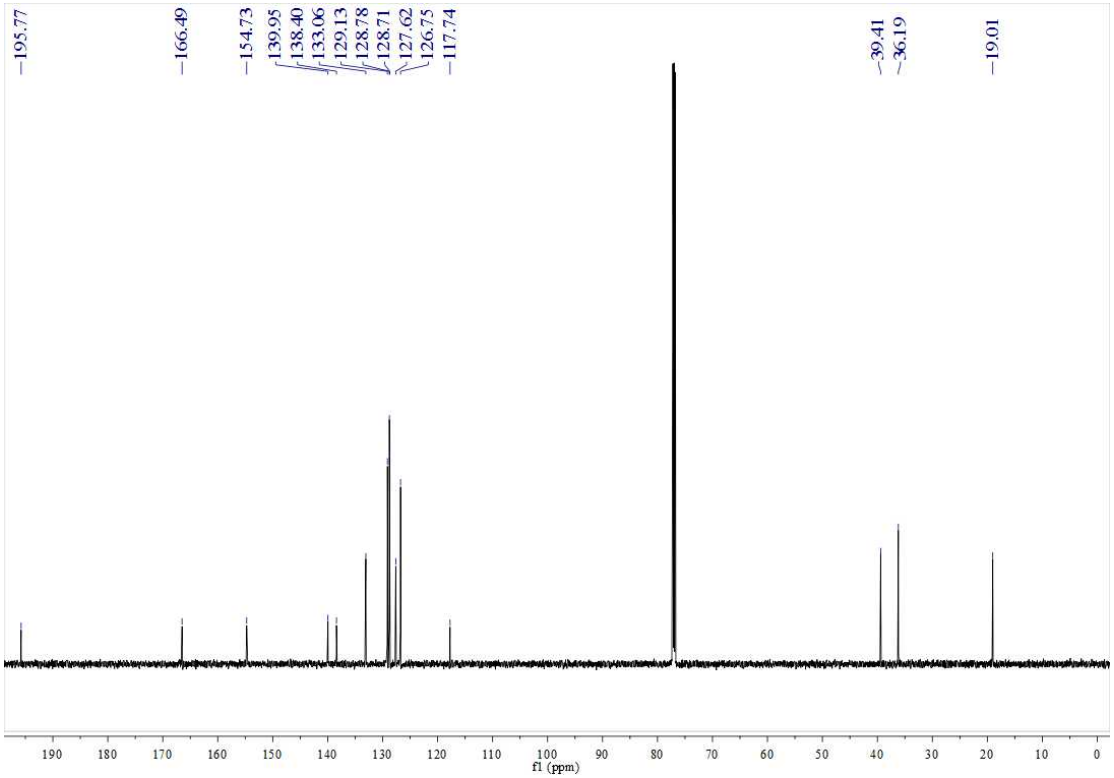


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	6.67	0.22	16.75	245.14	1.68
2	7.15	0.30	3.10	65.99	0.45
3	8.19	0.28	6.87	131.53	0.90
4	9.95	0.31	69.35	1468.18	10.05
5	14.19	0.45	419.45	12700.59	86.92
Total				14611.42	100.00

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

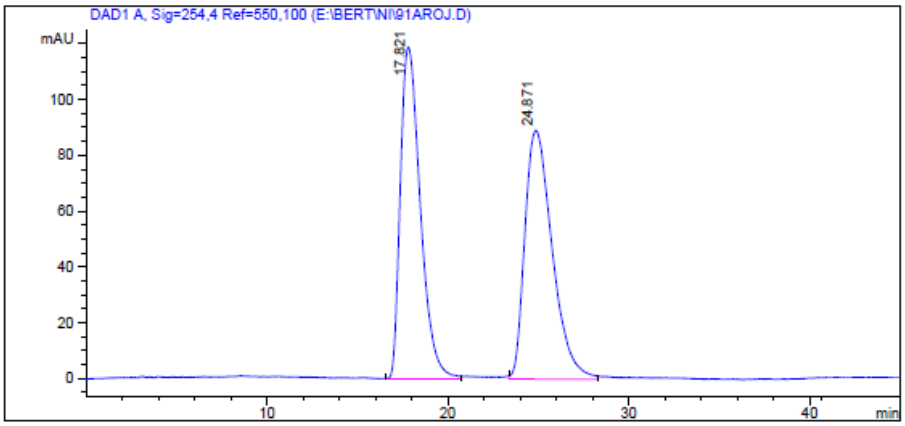


^{13}C NMR of **3f**



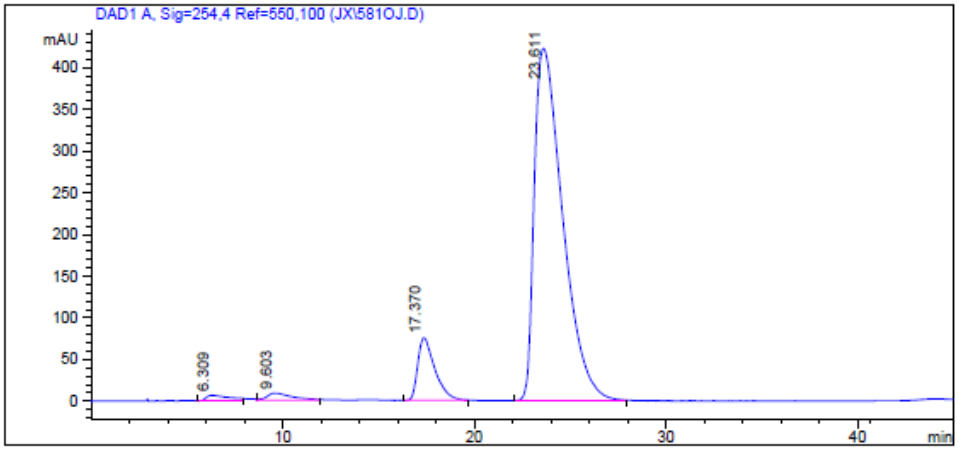
HPLC analysis: rac-**3f**

```
Sample Name:      Ni 91 A rac
Data file:        E:\BERT\NI\91AROJ.D
Sample Info:      Laufmittel: n-Heptan/EtOH 8:2;
                  Die Probe ist in DCM/LM gelöst


Säule:            DAICELOJ.M
Säuleninfo:       (250 x 4.6) mm 10µ

Operator:         Analytik Labor AKEN

Injektion Time:       13:05:15
Injektion Date:       10.10.2014

Instrument Conditions:   At Start              At Stop

Temperature in°C:         30.0                   30.0
Pressure in bar:          42.7                   41.4
Flow in ml/min:           1.0                    1.0
```



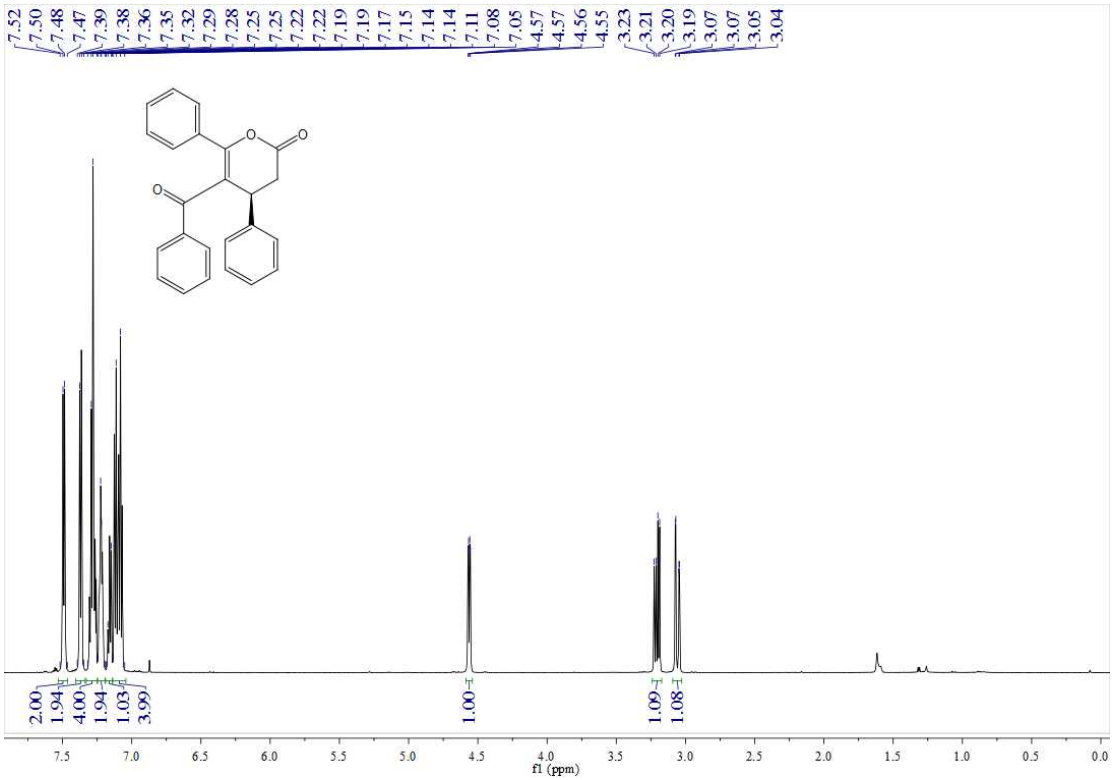
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	17.82	1.16	118.87	9111.51	49.25
2	24.87	1.58	89.12	9388.86	50.75
Total				18500.38	100.00

Enantioenriched **3f**

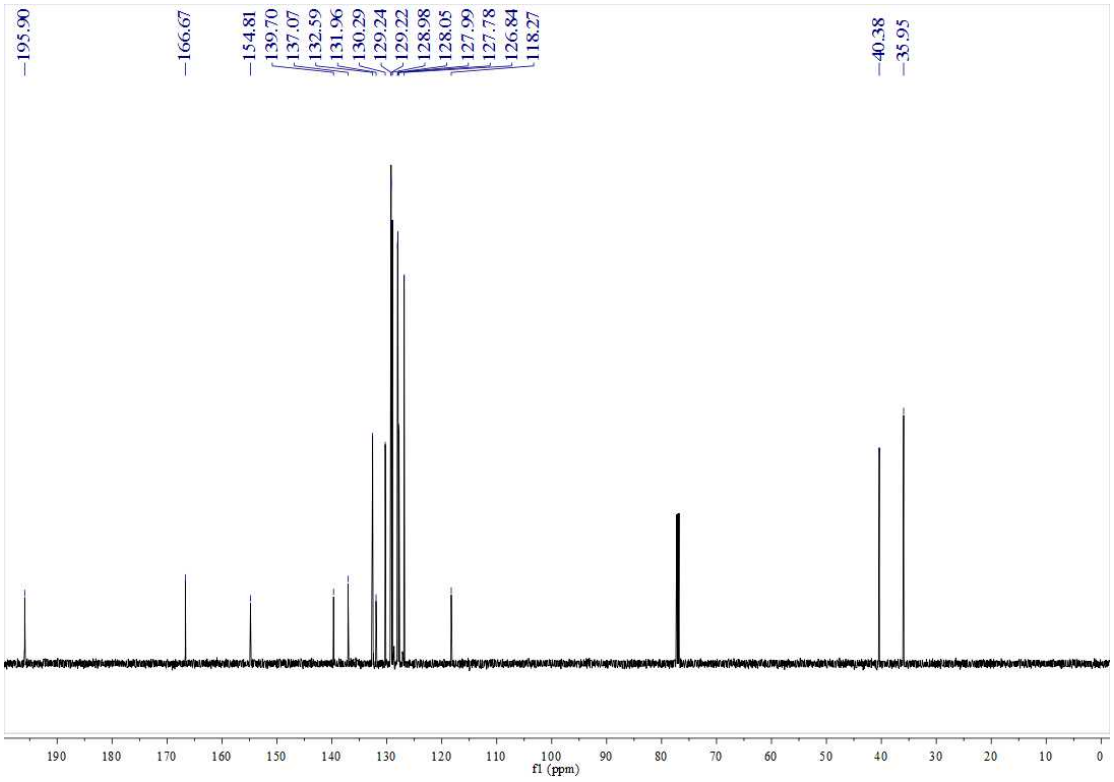


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	6.31	1.12	6.43	536.24	1.08
2	9.60	1.32	8.53	799.00	1.61
3	17.37	0.93	75.08	4677.73	9.45
4	23.61	1.55	422.18	43475.18	87.85
Total				49488.15	100.00

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

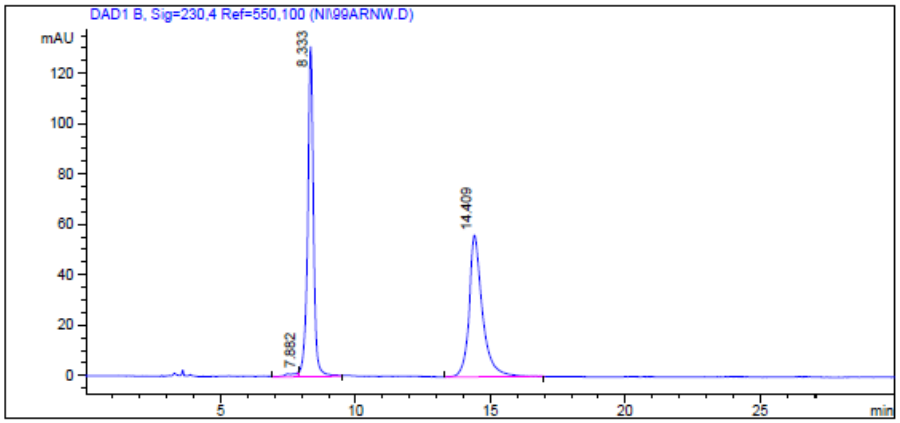


^{13}C NMR of **3g**



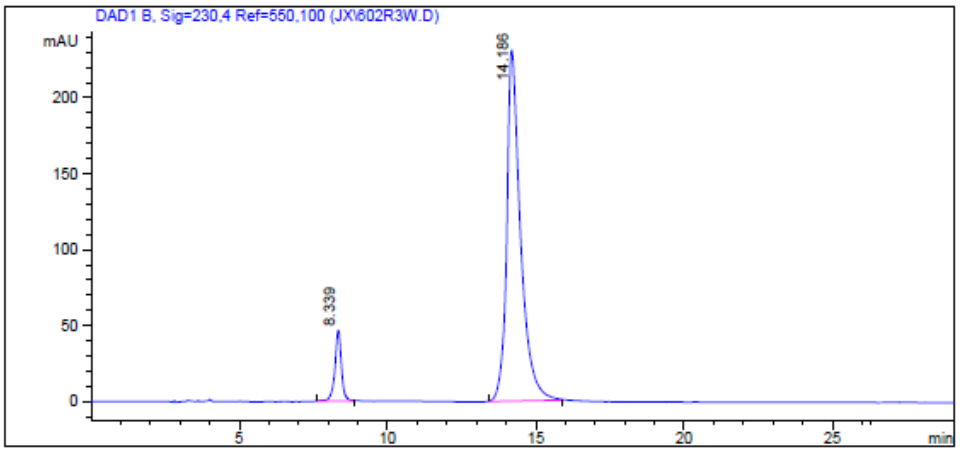
HPLC analysis: rac-**3g**

```
Data file:        D:\ERNIE\NI\99ARNW.D
Sample Info:      Laufmittel: n-Heptan/EtOH 7:3;
                  Die Probe ist in DCM/LM gelöst


Säule:            WHELK.M
Säuleninfo:       (250x4)mm

Operator:         Analytik Labor AKEN

Injektion Time:       11:28:47
Injektion Date:       27.02.2015

Instrument Conditions:    At Start              At Stop

Temperature in°C:         30.0                    30.0
Pressure in bar:          48.1                    48.1
Flow in ml/min:           0.7                     0.7
```



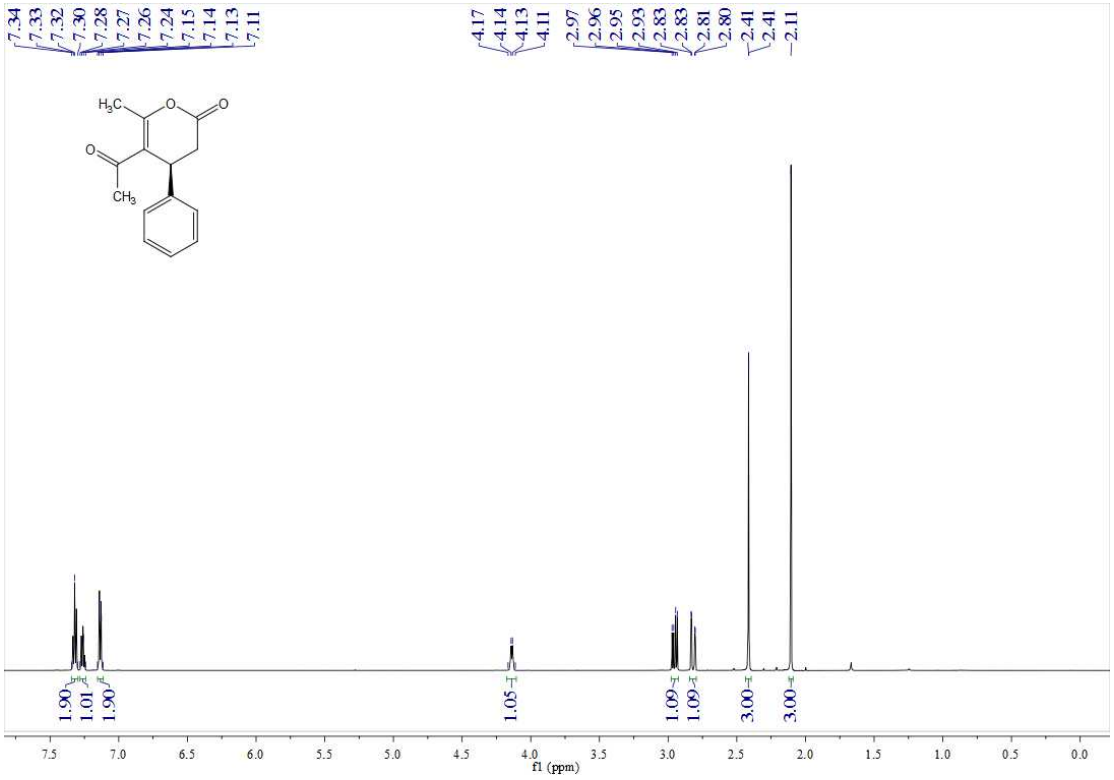
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	7.88	0.48	1.62	46.56	1.18
2	8.33	0.25	131.23	1969.85	49.93
3	14.41	0.57	56.27	1928.99	48.89
Total				3945.40	100.00

Enantioenriched **3g**

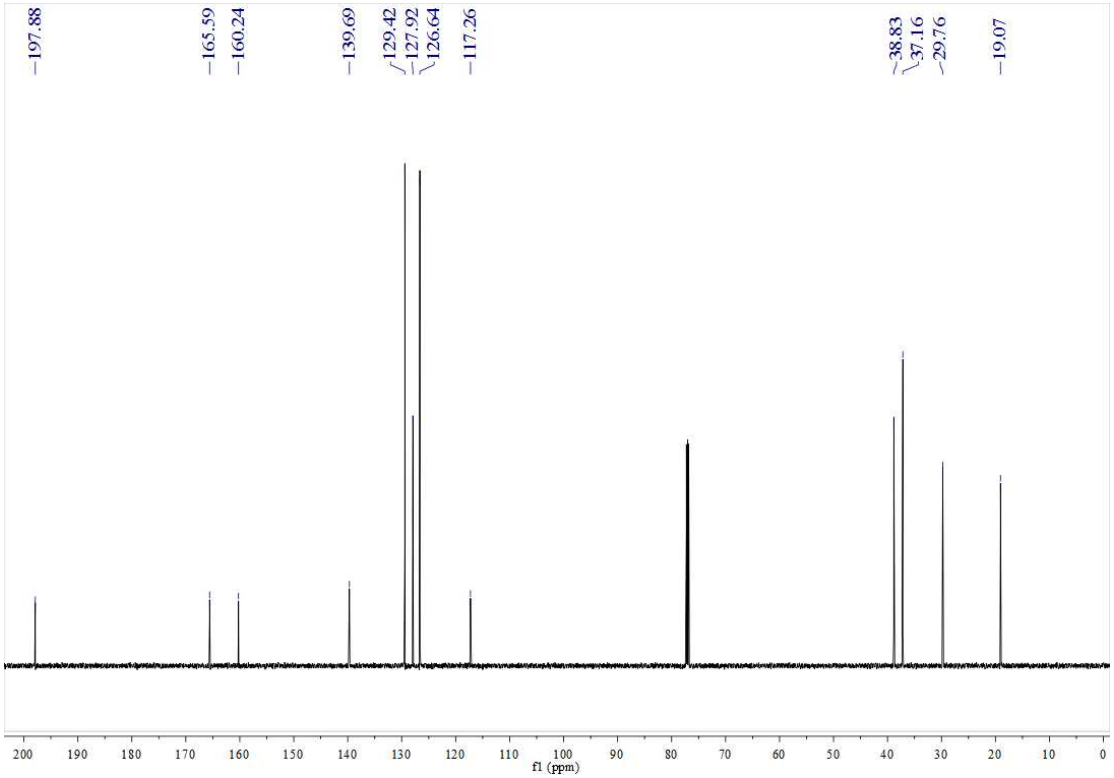


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.34	0.23	46.77	718.19	8.77
2	14.19	0.46	231.26	7474.65	91.23
Total				8192.84	100.00

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

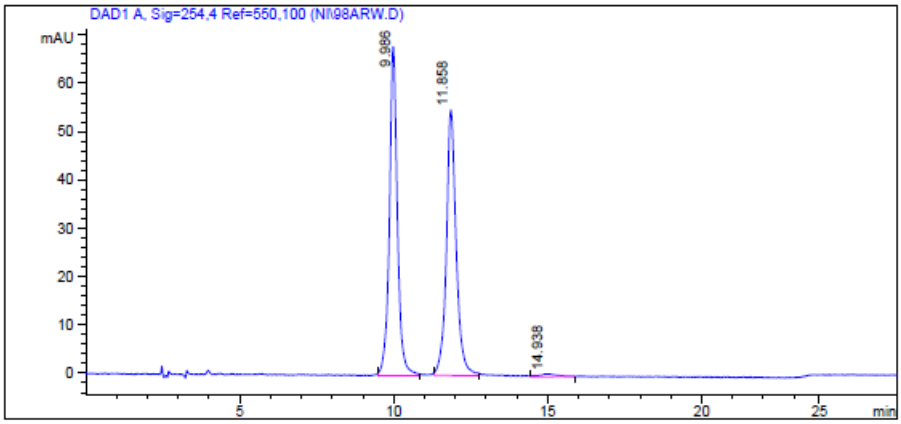


^{13}C NMR of **3h**



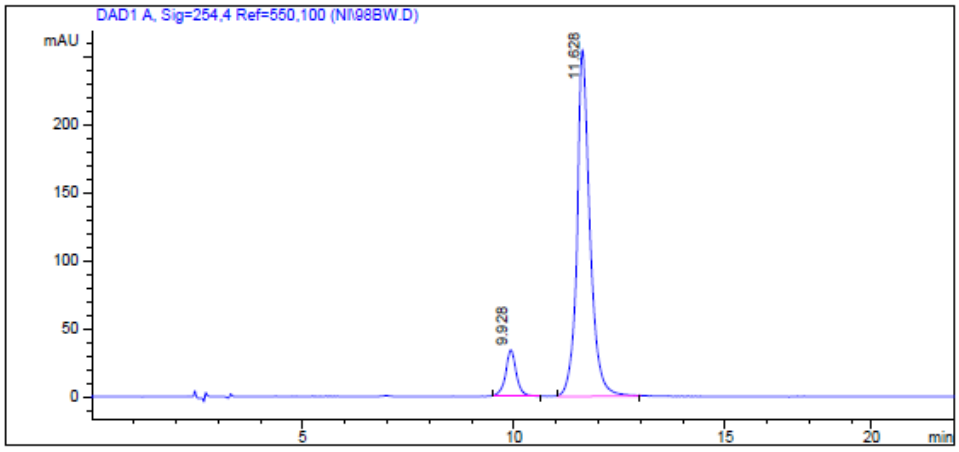
HPLC analysis: rac-**3h**

```
Data file:        D:\BERT\NI\98ARW.D
Sample Info:      Laufmittel: n-Heptan/EtOH 9:1;
                  Die Probe ist in DCM/LM gelöst


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

Operator:         Analytik Labor AKEN

Injektion Time:       10:23:16
Injektion Date:       14.01.2015

Instrument Conditions:    At Start              At Stop

Temperature in°C:         30.0                    30.0
Pressure in bar:          52.1                    51.6
Flow in ml/min:           1.0                     1.0
```



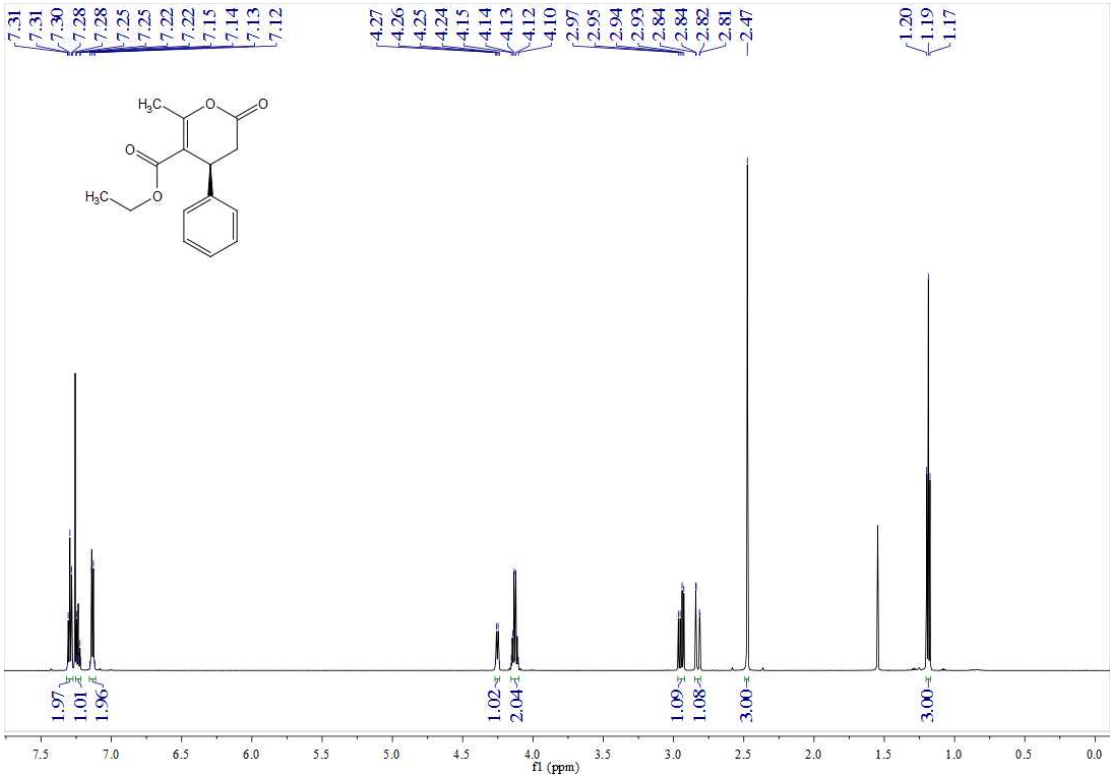
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	9.99	0.27	67.93	1225.23	49.68
2	11.86	0.33	54.97	1216.75	49.33
3	14.94	0.64	0.64	24.43	0.99
Total				2466.41	100.00

Enantioenriched **3h**

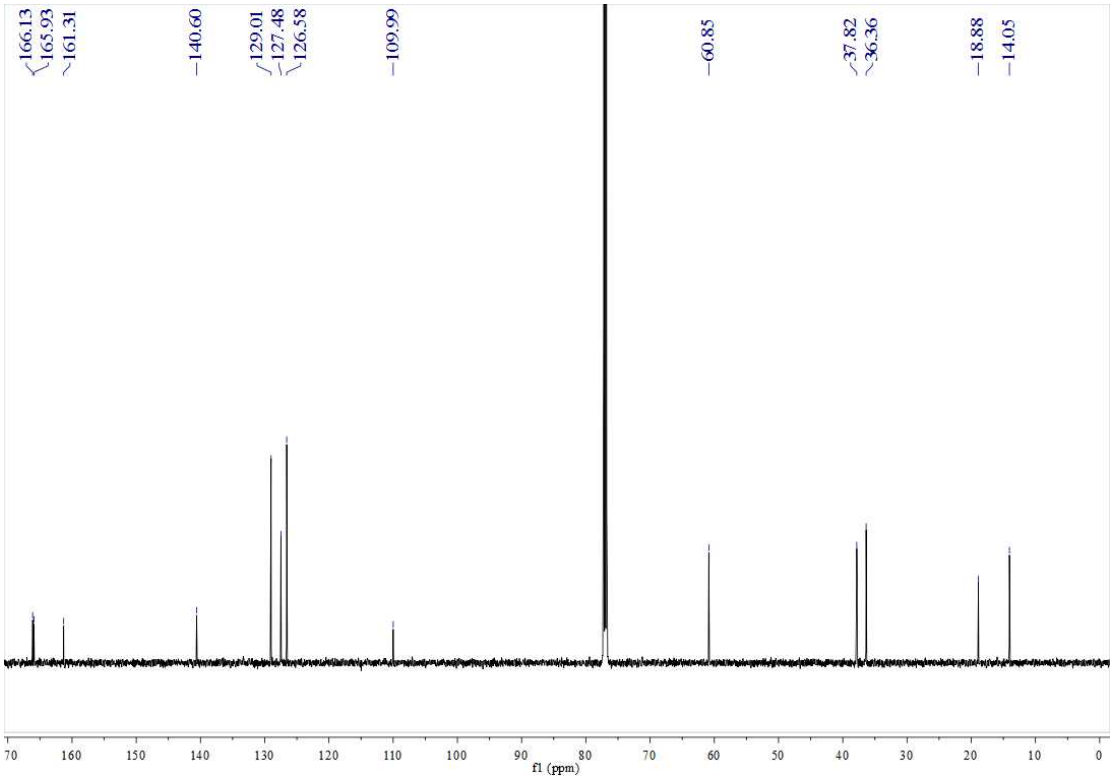


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	9.93	0.27	34.05	612.11	10.12
2	11.63	0.32	251.55	5437.39	89.88
Total				6049.50	100.00

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

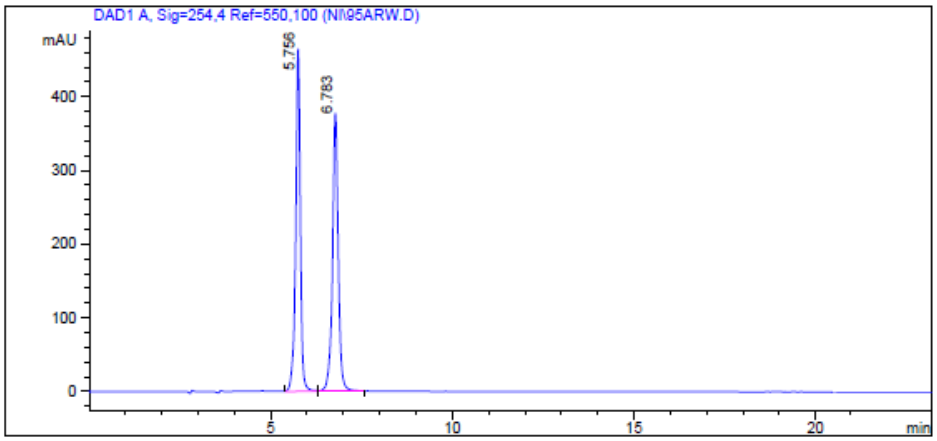


^{13}C NMR of **3i**



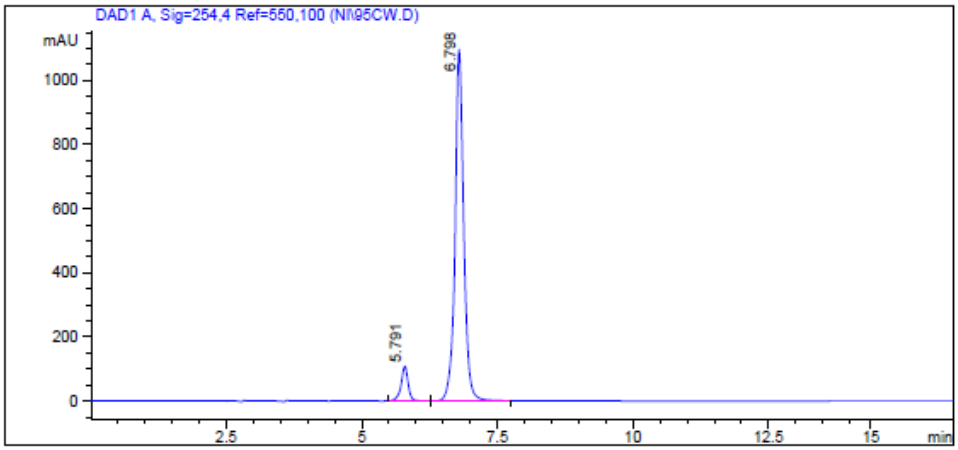
HPLC analysis: rac-**3i**

```
Data file:        D:\BERT\NI\95ARW.D
Sample Info:      Laufmittel: n-Heptan/EtOH 7:3;
                  Die Probe ist in DCM/LM gelöst


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

Operator:         Analytik Labor AKEN

Injektion Time:       09:54:50
Injektion Date:       09.01.2015

Instrument Conditions:    At Start              At Stop

Temperature in°C:         30.0                    30.0
Pressure in bar:          46.0                    45.7
Flow in ml/min:           0.7                     0.7
```



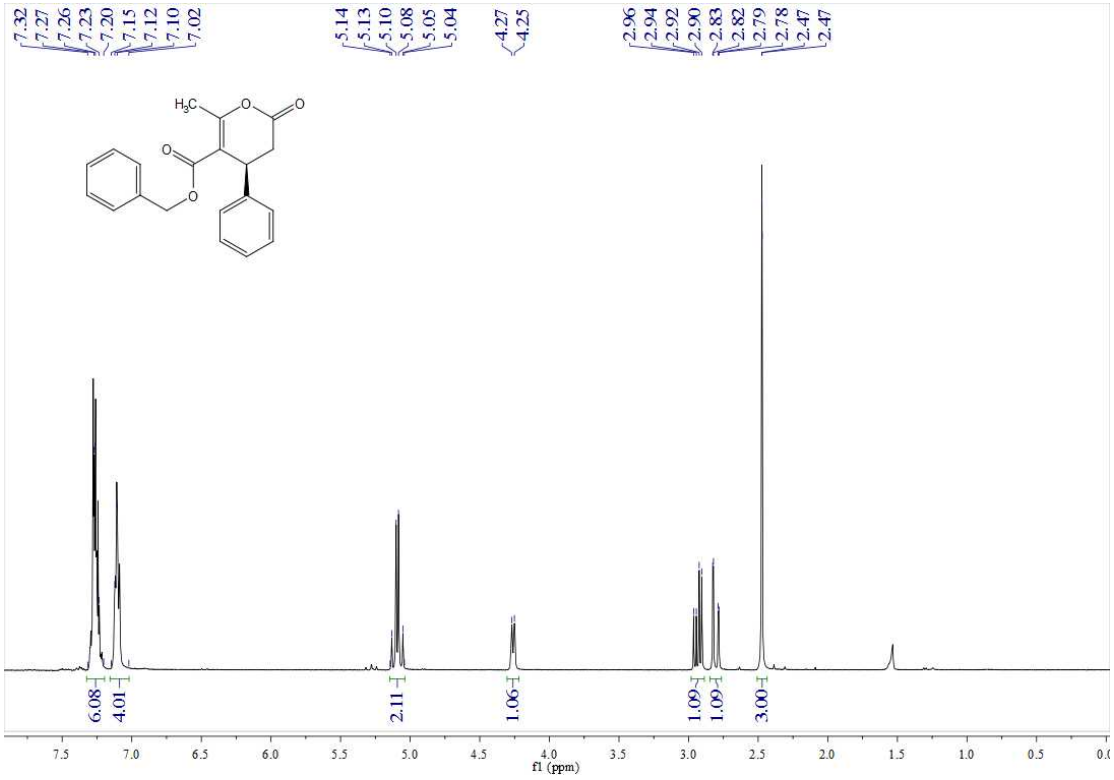
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.76	0.15	458.38	4175.62	49.90
2	6.78	0.18	371.93	4191.99	50.10
Total				8367.61	100.00

Enantioenriched **3i**

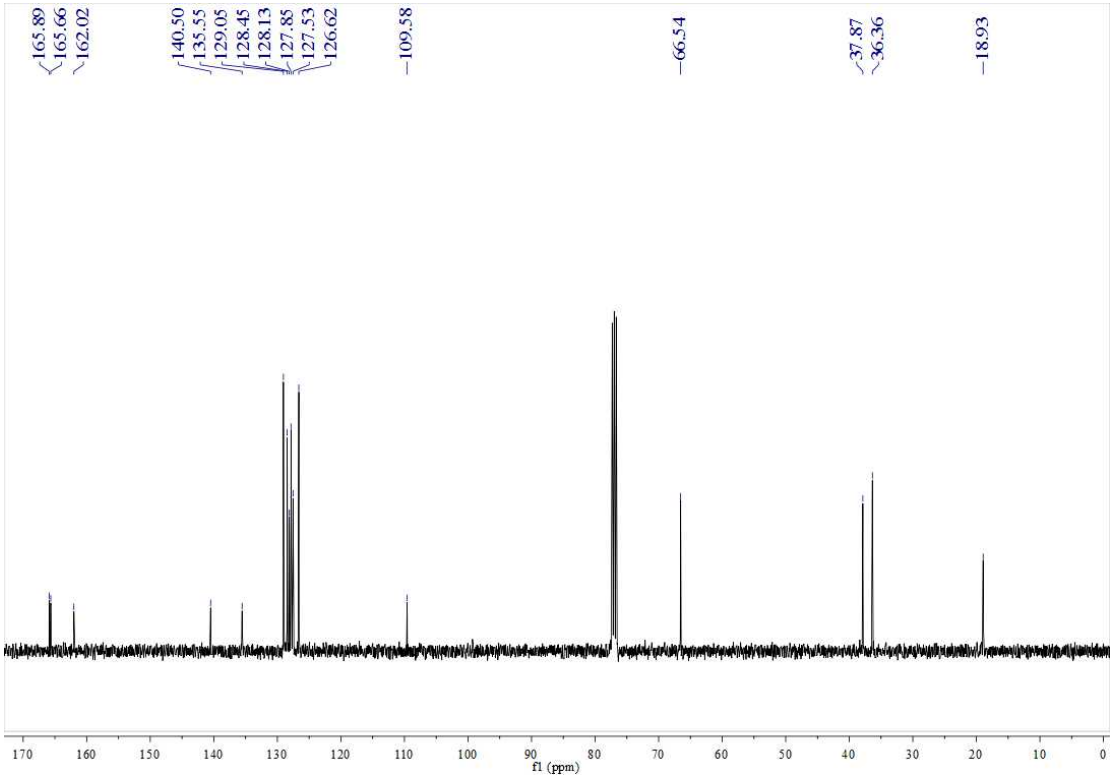


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.79	0.16	106.36	982.88	7.43
2	6.80	0.18	1095.33	12240.82	92.57
Total				13223.69	100.00

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

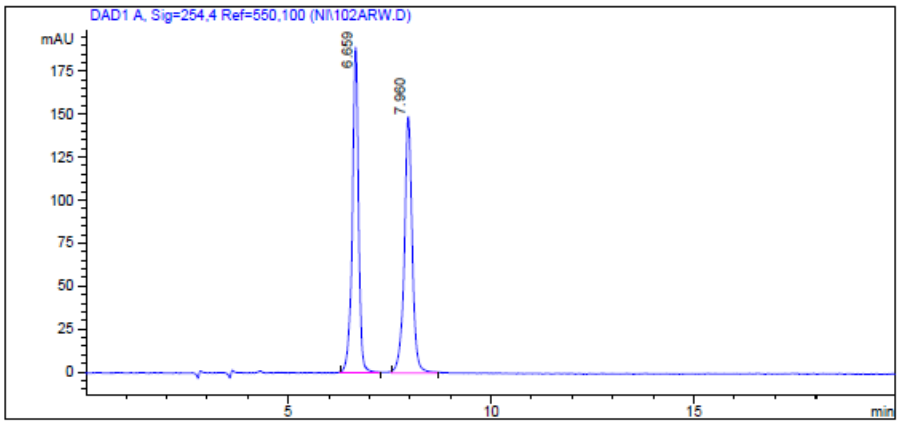


^{13}C NMR of **3j**



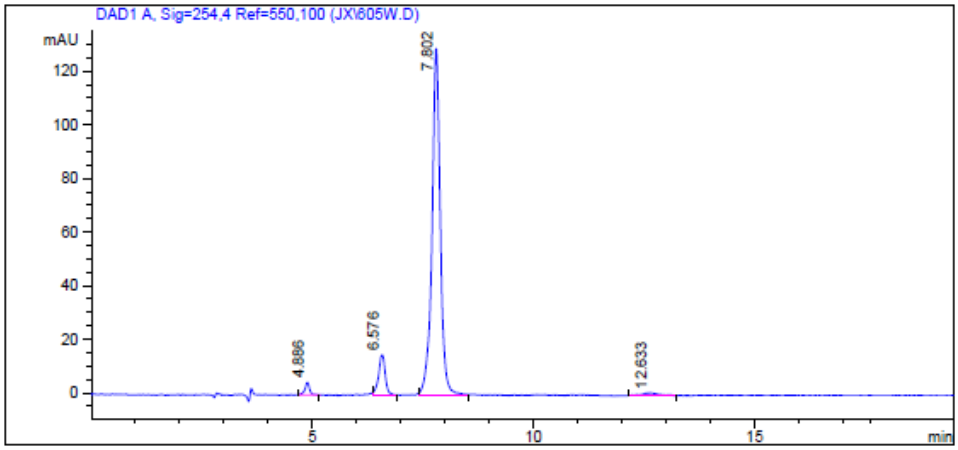
HPLC analysis: rac-**3j**

```
Data file:        D:\BERT\NI\102ARW.D
Sample Info:      Laufmittel: n-Heptan/EtOH 7:3;
                  Die Probe ist in DCM/LM gelöst


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

Operator:         Analytik Labor AKEN

Injektion Time:       08:28:01
Injektion Date:       23.01.2015

Instrument Conditions:    At Start              At Stop

Temperature in°C:         30.0                    30.0
Pressure in bar:          46.0                    45.9
Flow in ml/min:           0.7                     0.7
```



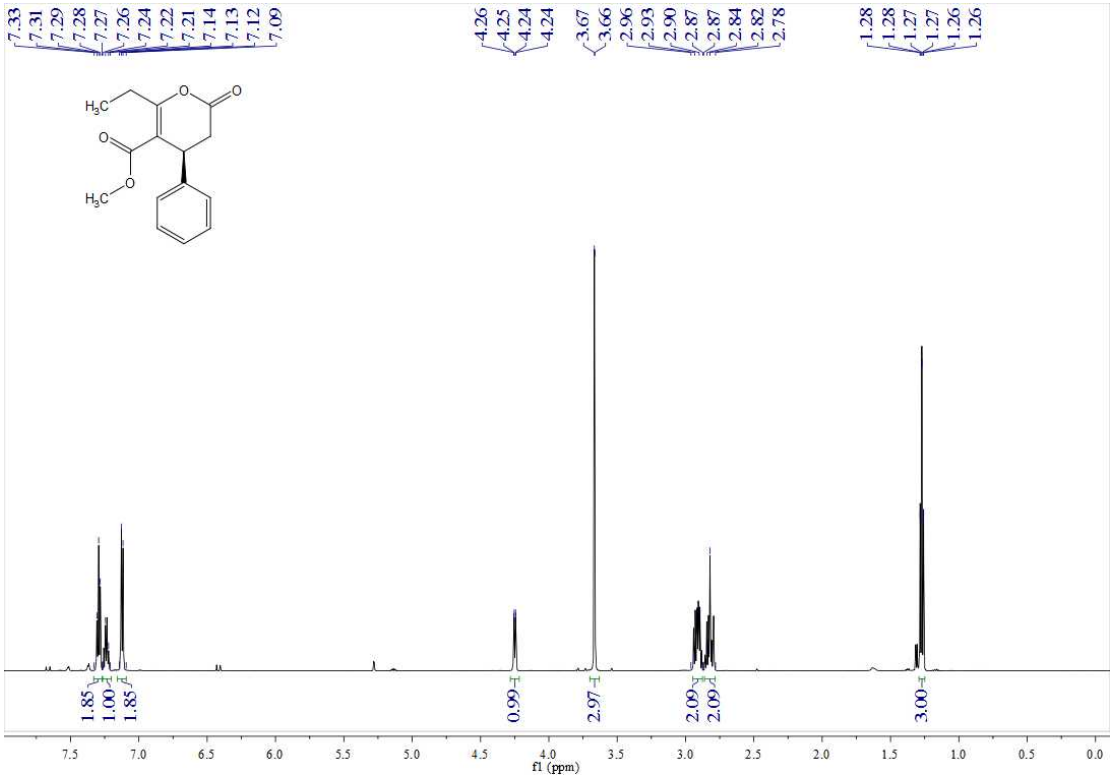
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	6.66	0.17	189.14	2037.55	50.09
2	7.96	0.22	148.08	2030.47	49.91
Total				4068.02	100.00

Enantioenriched **3j**

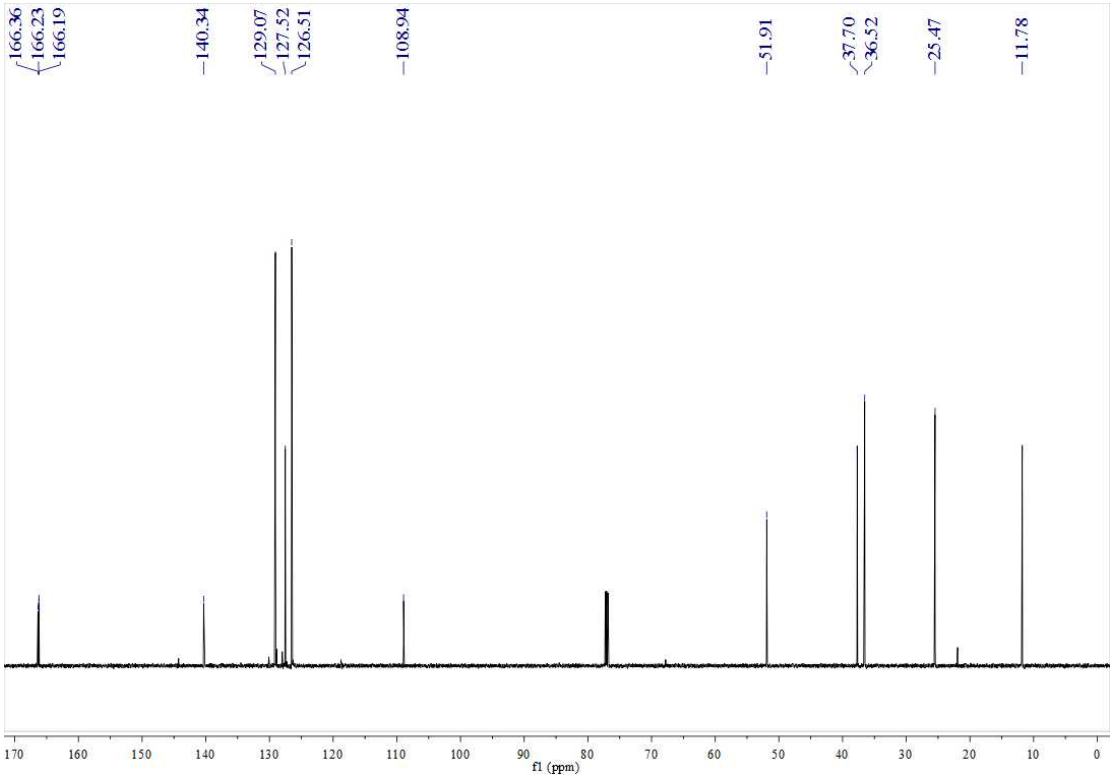


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.89	0.13	4.61	34.53	1.82
2	6.58	0.16	14.88	156.10	8.21
3	7.80	0.21	129.07	1689.22	88.85
4	12.63	0.34	0.93	21.34	1.12
Total				1901.19	100.00

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

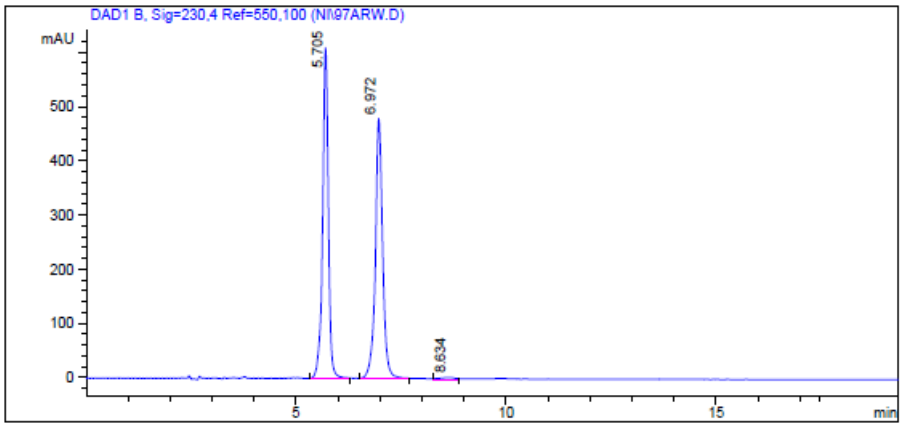


^{13}C NMR of **3k**



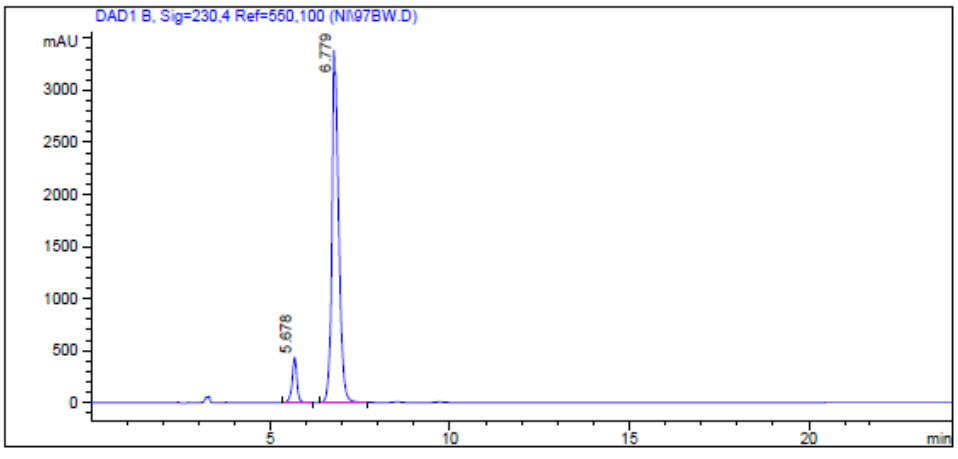
HPLC analysis: rac-**3k**

```
Data file:        D:\BERT\NI\97ARW.D
Sample Info:      Laufmittel: n-Heptan/EtOH 9:1;
                  Die Probe ist in DCM/LM gelöst


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

Operator:         Analytik Labor AKEN

Injektion Time:       09:59:55
Injektion Date:       14.01.2015

Instrument Conditions:    At Start              At Stop

Temperature in°C:         30.0                    30.0
Pressure in bar:          52.0                    52.0
Flow in ml/min:           1.0                     1.0
```



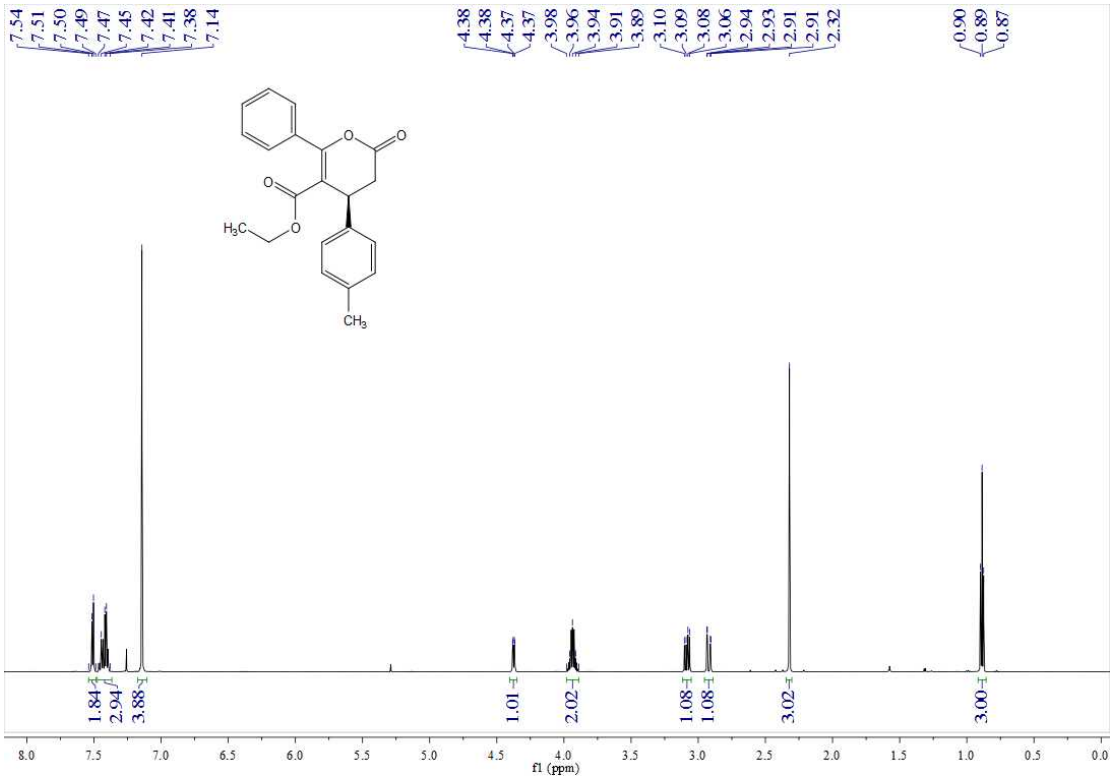
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.70	0.14	609.97	5753.59	49.57
2	6.97	0.18	478.98	5750.17	49.54
3	8.63	0.43	4.00	102.21	0.88
Total				11605.97	100.00

Enantioenriched **3k**

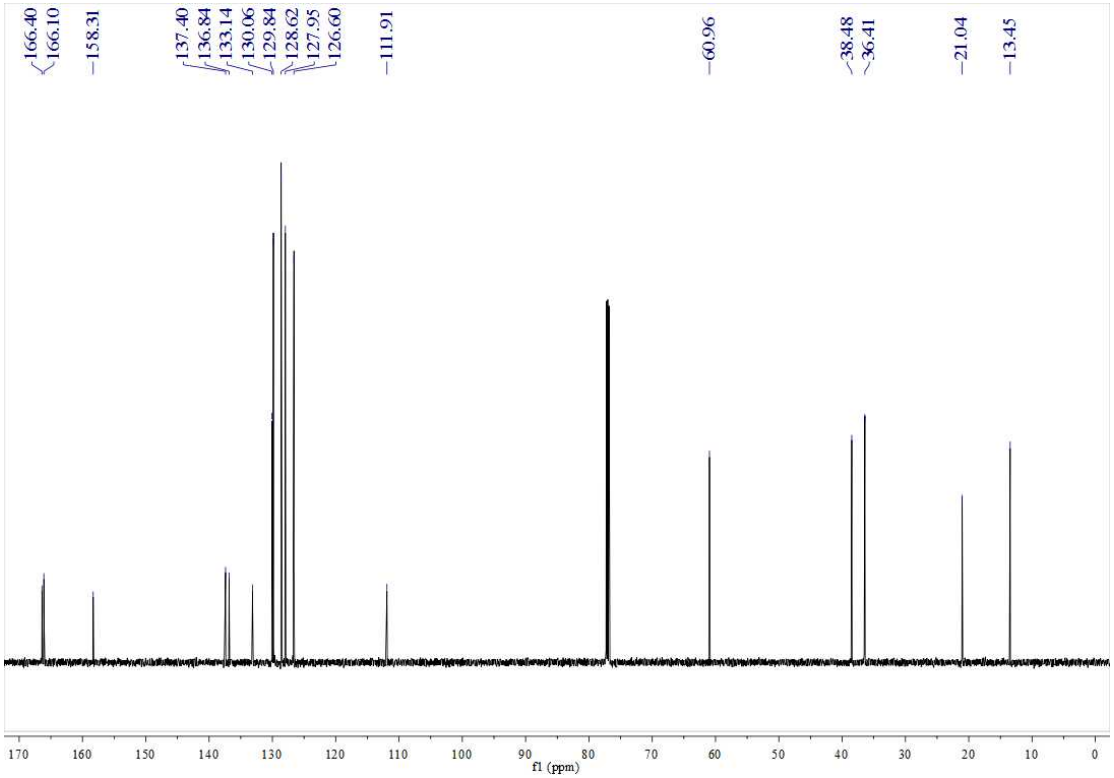


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.68	0.14	437.13	4070.50	8.40
2	6.78	0.17	3377.56	44406.45	91.60
Total				48476.95	100.00

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

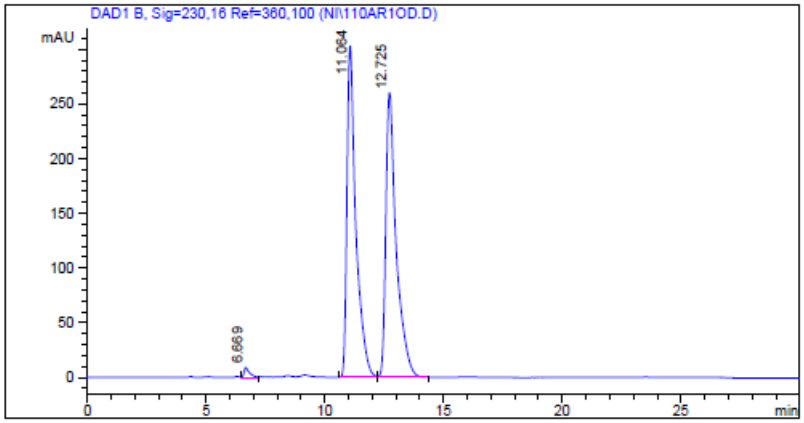


^{13}C NMR of **3l**



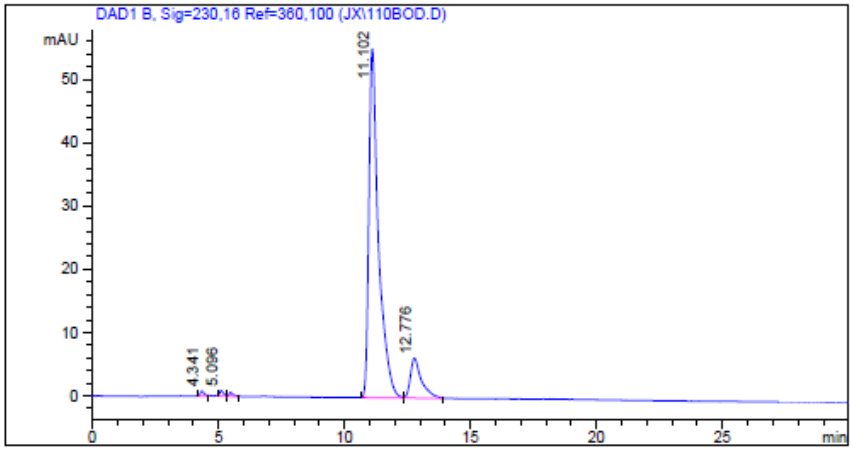
HPLC analysis: rac-**3l**

```
Data file:              D:\GONZO\NI\110AR1OD.D
Sample Info:            Laufmittel: n-Heptan/iPrOH  9:1;
                        Die Probe ist in DCM/LM gelöst

Säule:                  DAICELOD.M
Säuleninfo:             Chiralcel OD (250x4,6)mm
Operator:               Analytik Labor AKEN

 Injektion Time:         11:45:28
 Injektion Date:         03.02.2015

 Instrument Conditions:   At Start              At Stop
 Temperature in°C:          30.0°C                30.0°C
 Pressure in bar:           25.1                  24.8
 Flow in ml/min:            0.70                  0.70
```



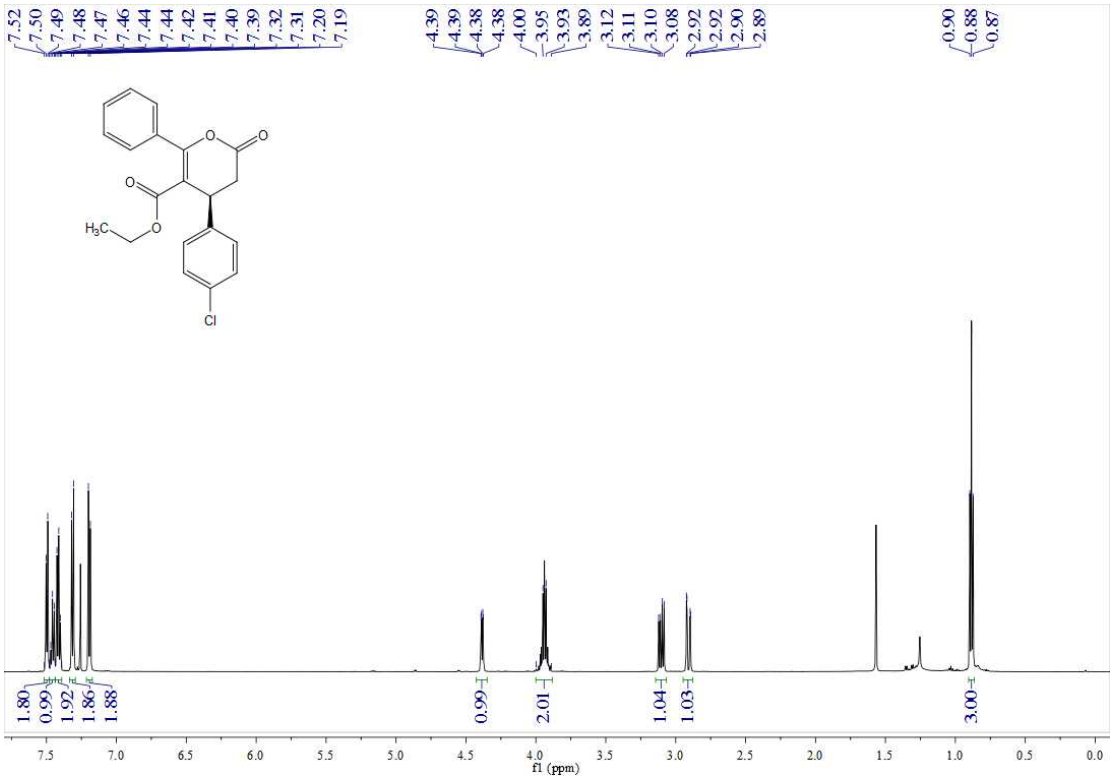
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	6.67	0.23	9.07	145.59	0.91
2	11.06	0.38	303.10	7919.58	49.43
3	12.72	0.44	260.29	7956.14	49.66
Total				16021.30	100.00

Enantioenriched **3l**

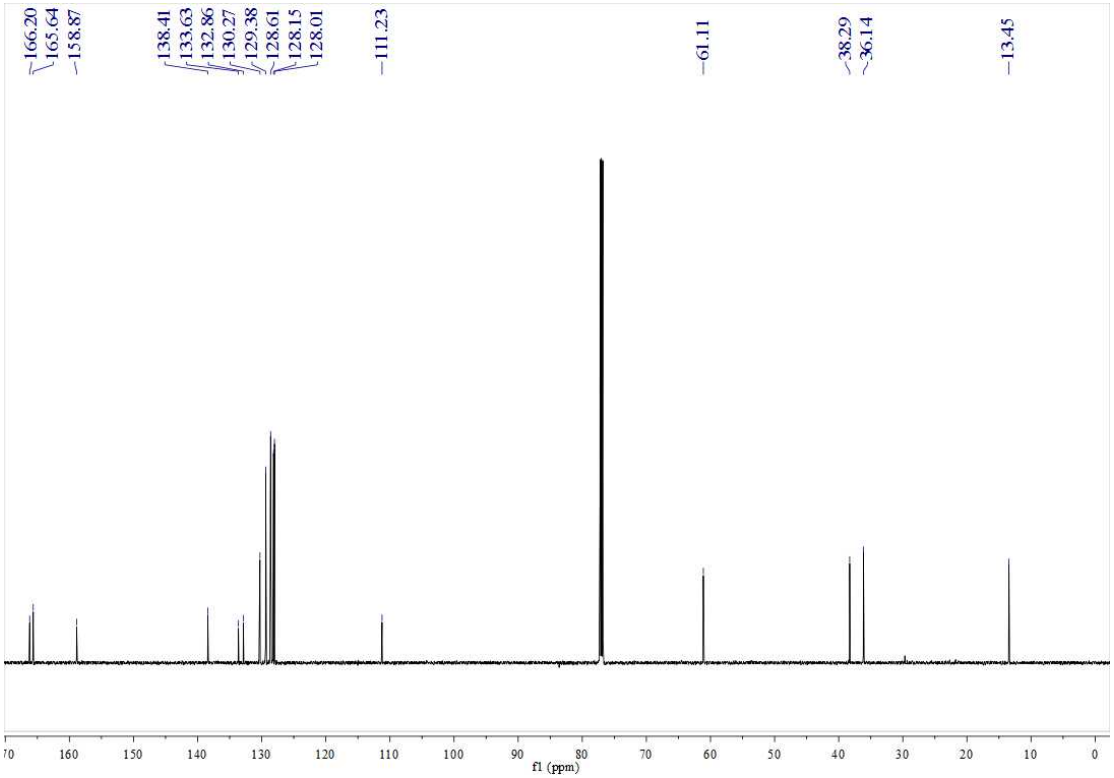


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.34	0.17	0.80	8.87	0.53
2	5.10	0.16	0.92	10.23	0.61
3	5.47	0.17	0.63	7.49	0.44
4	11.10	0.39	55.16	1464.45	86.93
5	12.78	0.44	6.32	193.52	11.49
Total				1684.55	100.00

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

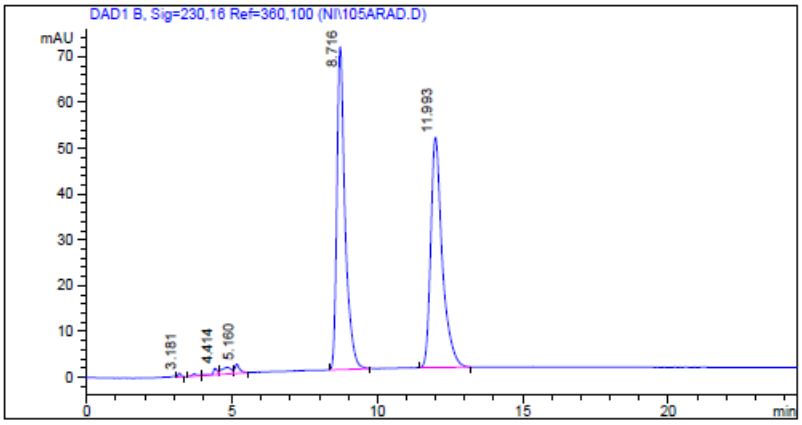


^{13}C NMR of **3m**



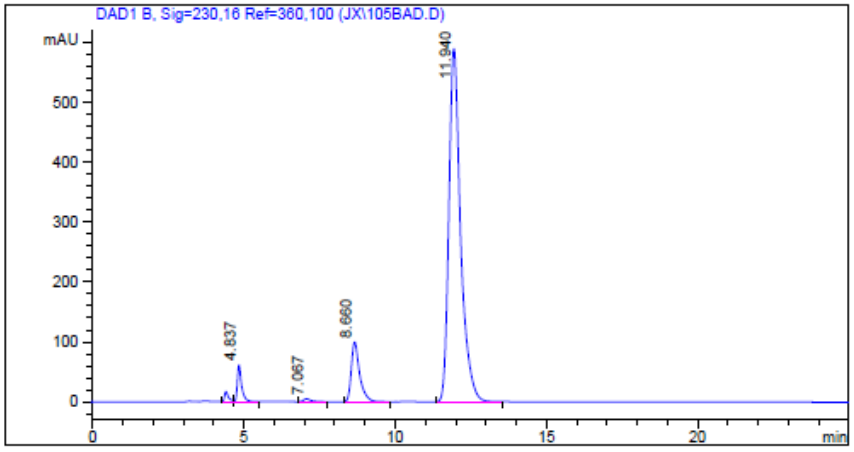
HPLC analysis: rac-**3m**

```
Data file:              D:\GONZO\NI\105ARAD.D
Sample Info:            Laufmittel: n-Heptan/iPrOH 9:1;
                        Die Probe ist in DCM/LM gelöst.

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

 Injektion Time:         07:50:49
 Injektion Date:         27.01.2015

 Instrument Conditions:   At Start              At Stop
 Temperature in°C:          30.0°C                30.0°C
 Pressure in bar:           32.5                  33.1
 Flow in ml/min:            1.00                  1.00
```



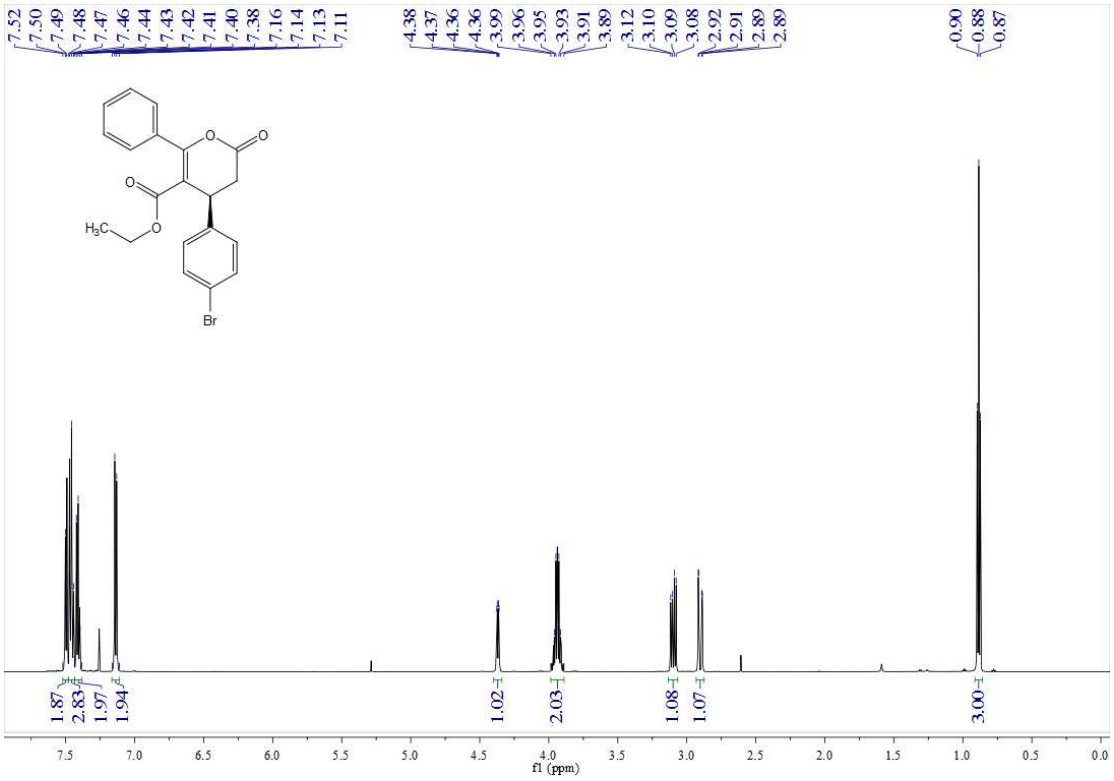
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.18	0.11	0.83	5.92	0.21
2	3.69	0.17	0.50	5.98	0.21
3	4.41	0.15	1.40	15.23	0.53
4	4.84	0.35	1.41	34.34	1.20
5	5.16	0.17	2.02	23.57	0.82
6	8.72	0.29	70.51	1387.88	48.55
7	11.99	0.41	50.24	1385.79	48.48
Total				2858.71	100.00

Enantioenriched **3m**

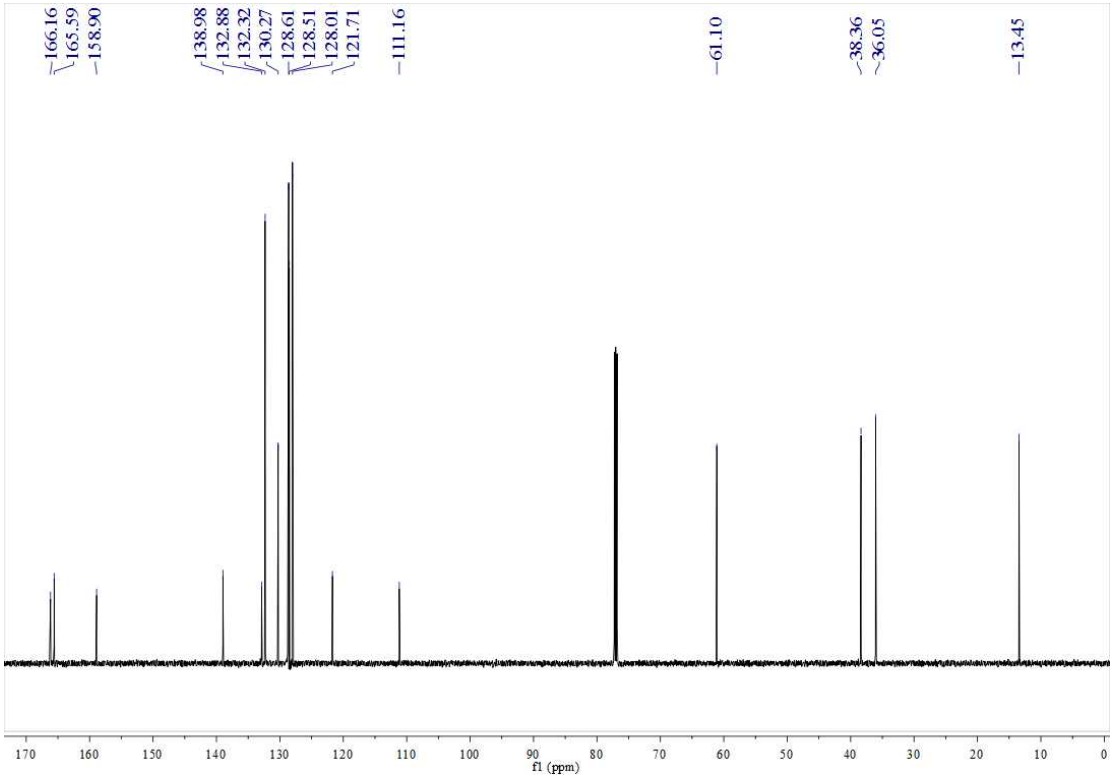


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.41	0.13	16.97	156.10	0.84
2	4.84	0.14	61.24	599.81	3.23
3	7.07	0.24	4.82	76.71	0.41
4	8.66	0.28	99.57	1903.06	10.25
5	11.94	0.40	589.74	15837.20	85.27
Total				18572.88	100.00

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

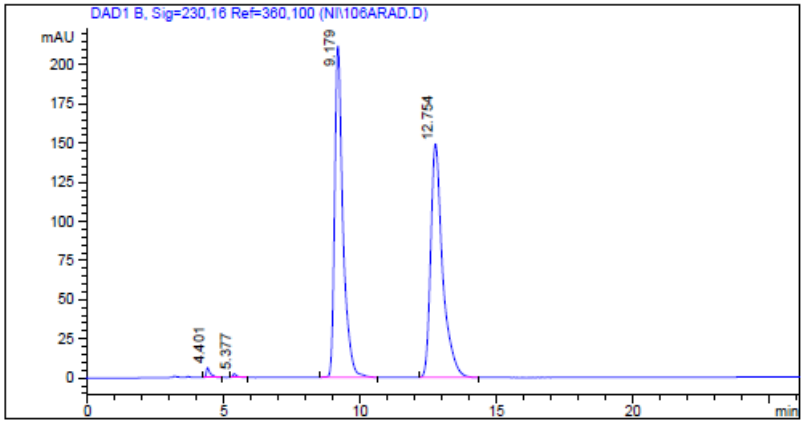


^{13}C NMR of **3n**



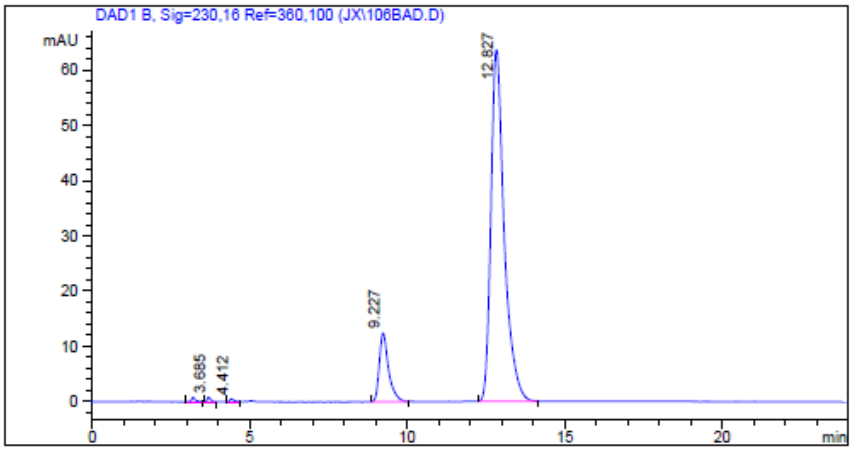
HPLC analysis: rac-**3n**

```
Data file:              D:\GONZO\NI\106ARAD.D
Sample Info:            Laufmittel: n-Heptan/iPrOH 9:1;
                        Die Probe ist in DCM/LM gelöst.

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

 Injektion Time:         08:19:00
 Injektion Date:         27.01.2015

 Instrument Conditions:   At Start              At Stop
 Temperature in°C:          30.0°C                30.0°C
 Pressure in bar:           32.4                  32.8
 Flow in ml/min:            1.00                  1.00
```



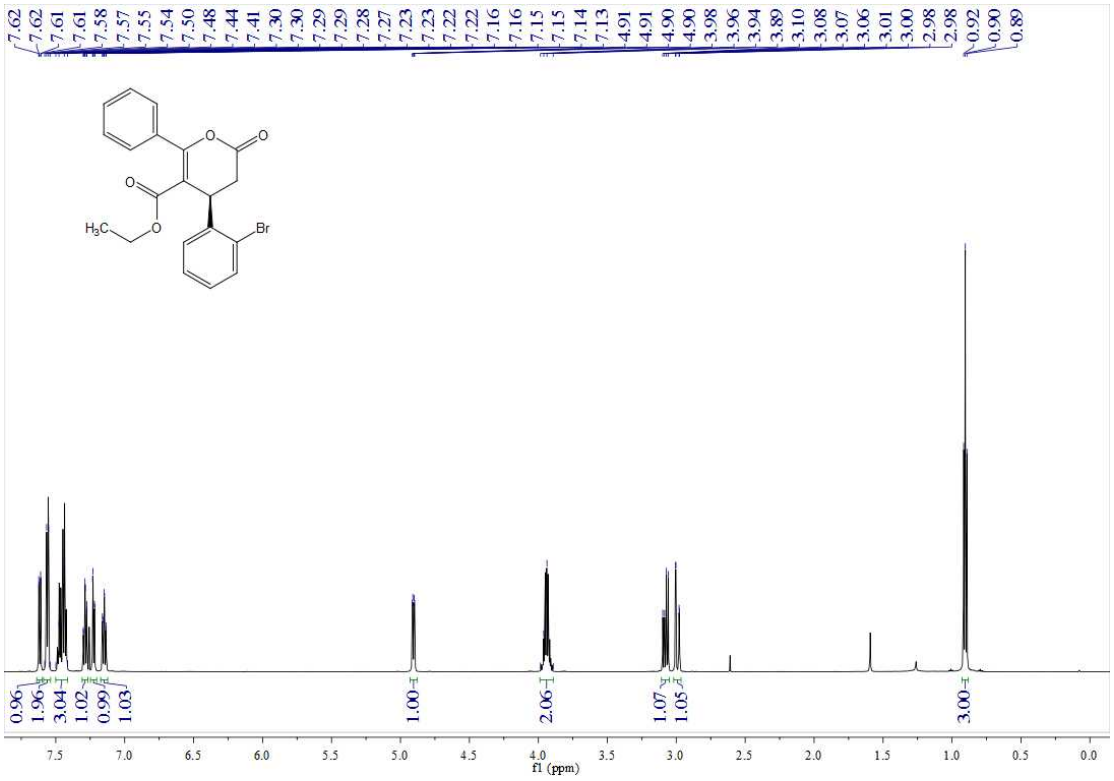
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.40	0.15	6.37	68.80	0.76
2	5.38	0.17	2.38	27.90	0.31
3	9.18	0.31	211.80	4477.86	49.26
4	12.75	0.45	149.06	4515.36	49.67
Total				9089.92	100.00

Enantioenriched **3n**

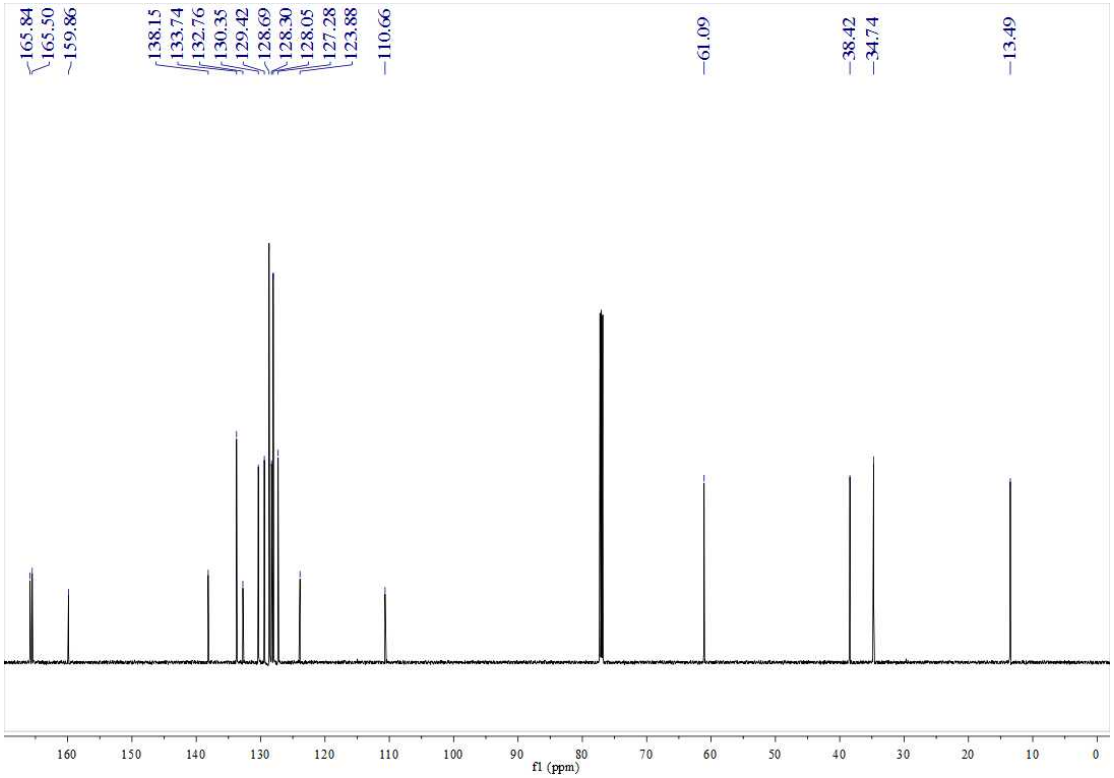


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.19	0.13	0.83	7.24	0.34
2	3.68	0.11	0.85	6.34	0.30
3	4.41	0.14	0.53	5.10	0.24
4	9.23	0.30	12.44	255.68	11.95
5	12.83	0.44	63.69	1864.46	87.17
Total				2138.82	100.00

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

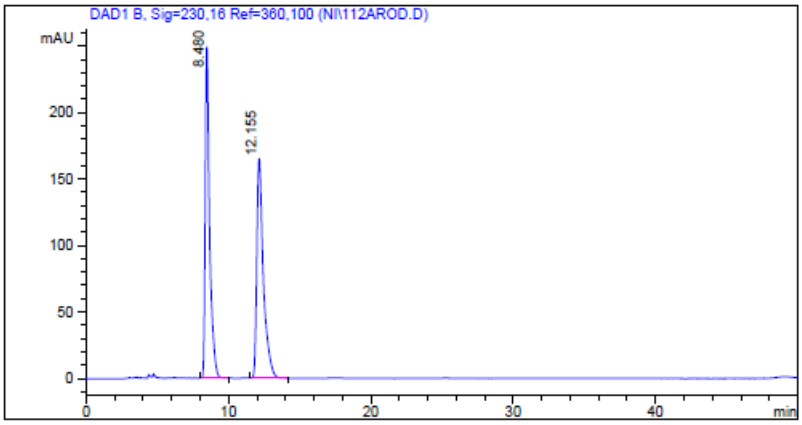


^{13}C NMR of **3o**



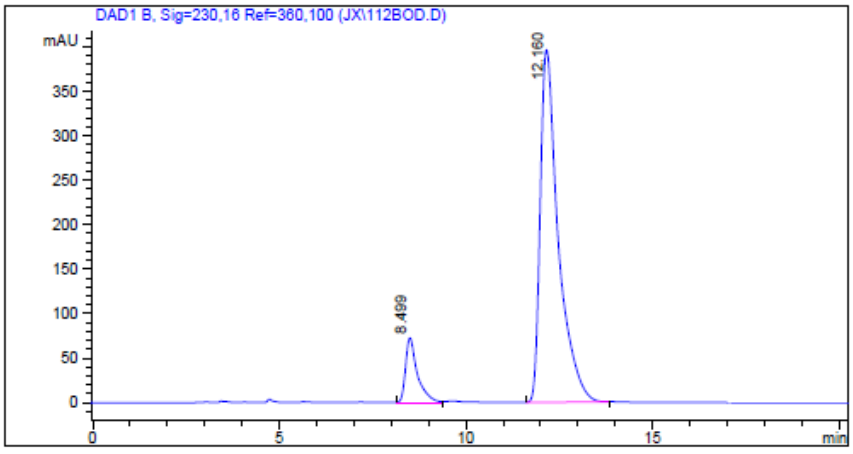
HPLC analysis: rac-**3o**

```
Data file:              D:\GONZO\NI\112AROD.D
Sample Info:            Laufmittel: n-Heptan/iPrOH  9:1;
                        Die Probe ist in DCM/LM gelöst

Säule:                  DAICELOD.M
Säuleninfo:             Chiralcel OD (250x4,6)mm
Operator:               Analytik Labor AKEN

 Injektion Time:         17:24:19
 Injektion Date:         02.02.2015

 Instrument Conditions:   At Start              At Stop
 Temperature in°C:          30.0°C                30.0°C
 Pressure in bar:           35.5                  35.8
 Flow in ml/min:            1.00                  1.00
```



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.48	0.32	247.92	5339.45	50.11
2	12.16	0.47	164.76	5316.61	49.89
Total				10656.06	100.00

Enantioenriched **3o**



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.50	0.32	72.56	1599.90	10.72
2	12.16	0.50	396.27	13318.11	89.28
Total				14918.01	100.00