Supporting Information

Synthesis of A New Spiro-BOX Ligand and Its Application in Enantioselective Allylic Cyclization Based on Carbopalladation of Allenylhydrazines

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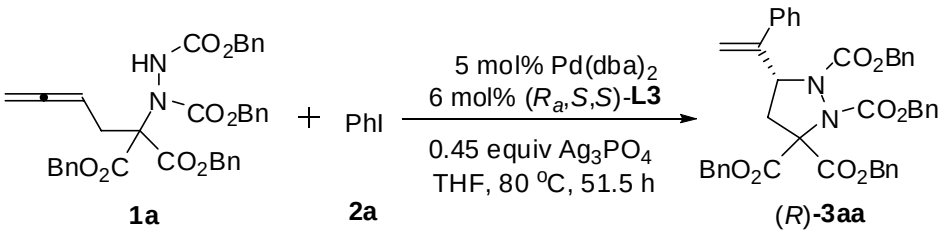
General Information. NMR spectra were taken with a Varian Mercury-300 (300 MHz for ^{1}H NMR, 75.4 MHz for ^{13}C NMR) and Varian Mercury-400 (400 MHz for ^{1}H NMR, 100.5 MHz for ^{13}C NMR) spectrometer in $CDCl_3$. Chemical shifts were recorded in ppm relative to TMS in $CDCl_3$ and coupling constants were reported in Hz. The high resolution mass spectra were recorded on a Finnigan MAT 8430 spectrometer. Other mass spectra were obtained on a Shimadzu GCMS-2010 or Shimadzu LCMS-2010 spectrometer. IR studies were carried out on a Perkin-Elmer 983 spectrometer. All reactions were carried out in a oven dried Schlenk tube with a screw cap under Ar atmosphere. THF, DME, and anisole were dried over sodium wire with benzophenone as the indicator and distilled freshly before use.

1. 1,2,3,3-Tetrakis(benzyloxycarbonyl)-5-(*R*)-(1'-phenylethenyl)pyrazolidine (*R*-3aa)

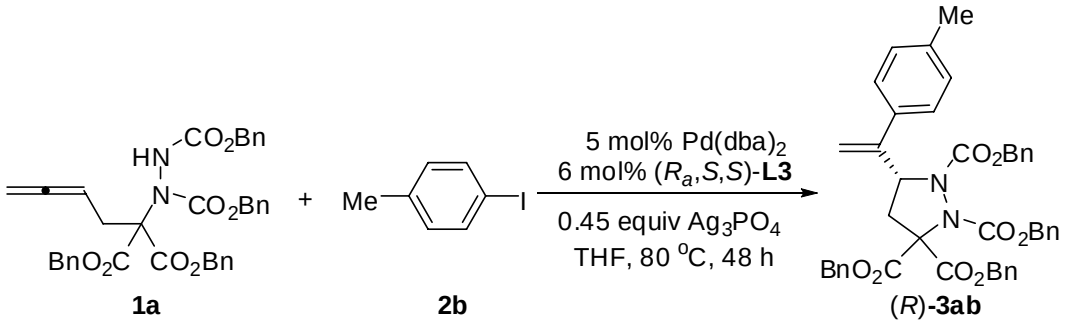


1a **2a** (*R*)-**3aa**

Typical Procedure: To a Schlenk tube with a screw cap were added $Pd(dba)_2$ (3 mg, 0.0053 mmol), (R_a,*S*,*S*)-**L3** (4 mg, 0.0063 mmol), and 1 mL of THF. The resulting mixture was stirred for 2 h at room temperature, which was followed by sequentially introduction of Ag_3PO_4 (19 mg, 0.045 mmol), **1a** (64 mg, 0.10 mmol), iodobenzene **2a** (25 mg, 0.12 mmol), and 1 mL of THF at rt. The resulting solution was stirred at

80 ^{o}C. When the reaction was completed as monitored by TLC, the solvent was evaporated under vacuum, and the residue was purified by chromatography on silica gel (eluent: petroleum ether : ethyl acetate = 5:1) to afford 61 mg of (*R*)-**3aa** (85%) as a vicous oil. 93% ee (determined by HPLC analysis (Chiralcel AD-H, hexane/*i*-PrOH = 80/20, 0.8 mL/min, 230 nm), tr 34.8 min (major), 37.9 min (minor)); $[\alpha]^{20}_{D}$ = - 5.2 (*c* = 0.95, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.06 (m, 21 H), 7.05-6.98 (m, 4 H), 5.55 (s, 1 H), 5.44-5.38 (m, 1 H), 5.13-4.78 (m, 9 H), 3.00 (dd, *J* = 13.2, 8.4 Hz, 1 H), 2.47 (dd, *J* = 13.2, 2.8 Hz, 1 H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 167.8, 166.0, 157.0, 153.3, 143.6, 138.4, 135.5, 135.3, 134.9, 134.4, 128.40, 128.36, 128.2, 128.15, 128.12, 128.07, 128.0, 127.8, 127.6, 126.6, 113.7, 72.2, 68.5, 68.3, 68.2, 68.0, 61.3, 41.3; MS (ESI): *m/z* 749 ($M+K^+$), 733 ($M+Na^+$); IR (neat): 1738, 1586, 1498, 1455, 1397, 1337, 1276, 1189, 1104, 1069 cm^{-1}; HRMS calcd. for $C_{43}H_{39}N_2O_8$ [M^++1]: 711.2701; Found: 711.2735.

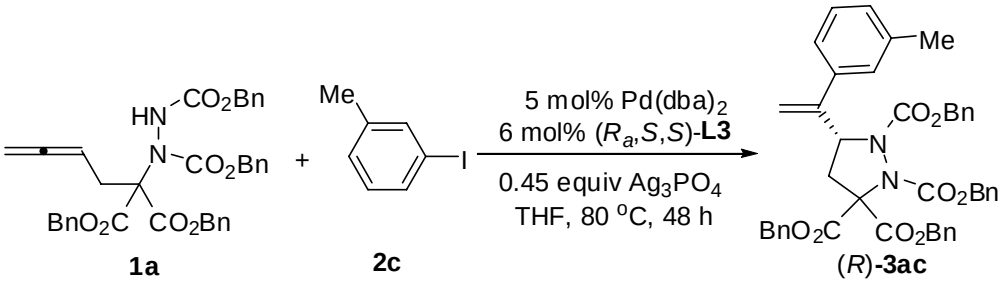
2. 1,2,3,3-Tetrakis(benzyloxycarbonyl)-5-(*R*)-(1'-(4"-methylphenyl)ethenyl-pyrazolidine (*R*-3ab)



The reaction of $Pd(dba)_2$ (3 mg, 0.0053 mmol), (R_a,*S*,*S*)-**L3** (4 mg, 0.0063 mmol),

Ag_3PO_4 (19 mg, 0.045 mmol), **1a** (64 mg, 0.10 mmol), **2b** (26 mg, 0.12 mmol) afforded 52 mg (71%) of (*R*)-**3ab** as a viscous oil. 93% ee (determined by HPLC analysis (Chiralcel OD-H, hexane/*i*-PrOH = 60/40, 0.7 mL/min, 214 nm), tr 6.3 min (major), 7.9 min (minor)); $[\alpha]^{20}{}_{D}$ = - 8.0 (*c* = 1.25, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.07 (m, 18 H), 7.01-6.91 (m, 6 H), 5.51 (s, 1 H), 5.42-5.37 (m, 1 H), 5.11-4.78 (m, 9 H), 2.99 (dd, *J* = 13.6, 8.8 Hz, 1 H), 2.49 (dd, *J* = 13.6, 3.2 Hz, 1 H), 2.23 (s, 3 H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 167.8, 166.0, 157.0, 153.3, 143.4, 137.6, 135.6, 135.5, 135.4, 134.9, 134.5, 129.1, 128.41, 128.37, 128.3, 128.2, 128.14, 128.09, 128.06, 127.9, 127.6, 126.4, 112.9, 72.2, 68.4, 68.25, 68.15, 68.0, 61.3, 41.4, 21.0; MS (ESI): *m/z* 763 ($M+K^+$), 747 ($M+Na^+$), 725 (M^++1); IR (neat): 1738, 1609, 1586, 1513, 1498, 1455, 1399, 1337, 1275, 1191, 1100, 1069, 1003 cm^{-1}; HRMS calcd. for $C_{44}H_{40}N_2O_8Na$ [$M+Na^+$]: 747.2677; Found: 747.2704.

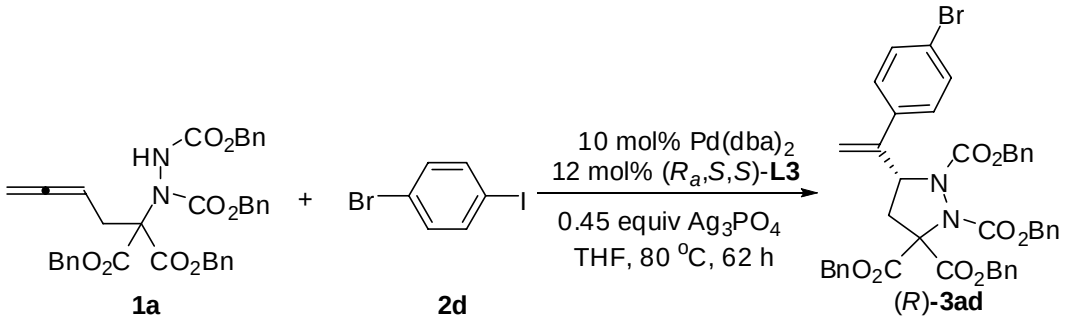
3. 1,2,3,3-Tetrakis(benzyloxycarbonyl)-5-(*R*)-(1'-(3''-methylphenyl)ethenyl)-pyrazolidine (*R*-3ac)



The reaction of $Pd(dba)_2$ (3 mg, 0.0053 mmol), (R_a,*S*,*S*)-**L3** (4 mg, 0.0063 mmol), Ag_3PO_4 (19 mg, 0.45 mmol), **1a** (66 mg, 0.10 mmol), **2c** (26 mg, 0.12 mmol) afforded 68 mg (90%) of (*R*)-**3ac** as a viscous oil. 92% ee (determined by HPLC analysis

(Chiralcel OD-H, hexane/*i*-PrOH = 80/20, 0.7 mL/min, 214 nm), tr 8.0 min (major), 10.2 min (minor)); $[\alpha]^{20}_{D}$ = - 5.2 (*c* = 1.20, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.07 (m, 18 H), 7.04 (d, *J* = 7.6 Hz, 1 H), 7.02-6.96 (m, 3 H), 6.88 (s, 1 H), 6.84 (d, *J* = 7.6 Hz, 1 H), 5.54 (s, 1 H), 5.44-5.39 (m, 1 H), 5.13-4.78 (m, 9 H), 3.00 (dd, *J* = 13.2, 8.8 Hz, 1 H), 2.49 (dd, *J* = 13.2, 2.4 Hz, 1 H), 2.19 (s, 3 H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 167.8, 166.0, 157.0, 153.3, 143.7, 138.4, 138.0, 135.6, 135.4, 134.9, 134.5, 128.6, 128.42, 128.36, 128.3, 128.2, 128.15, 128.12, 128.07, 128.0, 127.6, 127.2, 123.7, 113.4, 72.2, 68.5, 68.3, 68.2, 68.0, 61.3, 41.4, 21.4; MS (ESI): *m/z* 763 ($M+K^+$), 747 ($M+Na^+$); IR (neat): 1739, 1602, 1585, 1498, 1455, 1398, 1338, 1274, 1187, 1069 cm^{-1}; HRMS calcd. for $C_{44}H_{40}N_2O_8Na$ [$M+Na^+$]: 747.2677; Found: 747.2701.

4. 1,2,3,3-Tetrakis(benzyloxycarbonyl)-5-(*R*)-(1'-(4''-bromophenyl)ethenyl)-pyrazolidine (*R*-3ad)

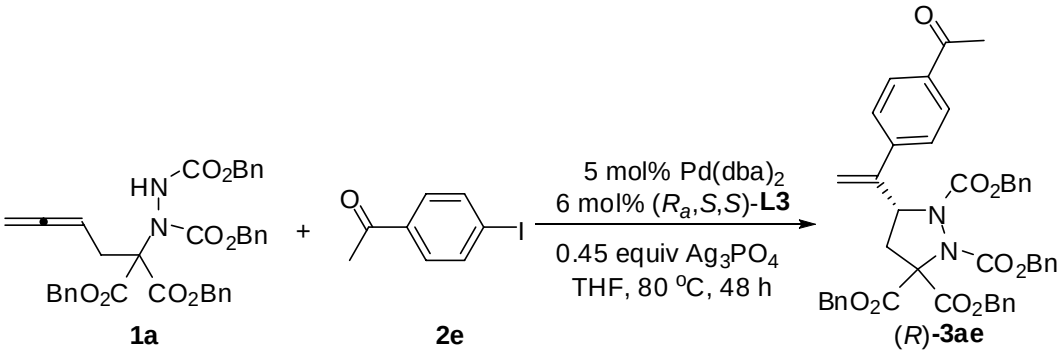


The reaction of $Pd(dba)_2$ (5 mg, 0.0088 mmol), (R_a,*S*,*S*)-**L3** (7 mg, 0.011 mmol), Ag_3PO_4 (19 mg, 0.45 mmol), **1a** (61 mg, 0.096 mmol), **2d** (34 mg, 0.12 mmol) afforded 63 mg (83%) of (*R*)-**3ad** as a viscous oil. 93% ee (determined by HPLC

analysis (Chiralcel AD-H, hexane/*i*-PrOH = 60/40, 0.7 mL/min, 214 nm), tr 16.2 min (major), 27.4 min (minor)); $[\alpha]^{20}{}_{D}$ = - 11.5 (*c* = 1.10, EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.07 (m, 20 H), 7.01-6.96 (m, 2 H), 6.87-6.82 (m, 2 H), 5.55 (s, 1 H), 5.38-5.32 (m, 1 H), 5.13-4.90 (m, 6 H), 4.86-4.76 (m, 3 H), 2.99 (dd, *J* = 13.5, 8.7 Hz, 1 H), 2.42 (dd, *J* = 13.5, 2.7 Hz, 1 H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 167.6, 165.9, 157.0, 153.2, 142.8, 137.4, 135.5, 135.3, 134.8, 134.4, 131.5, 128.5, 128.43, 128.40, 128.37, 128.23, 128.19, 128.1, 128.0, 127.6, 121.8, 114.5, 72.2, 68.5, 68.3, 68.2, 68.1, 61.1, 41.2; MS (ESI): *m/z* 829 (M(^{81}Br)+K^+), 827 (M(^{79}Br)+K^+), 813 (M(^{81}Br)+Na^+), (811 (M(^{79}Br)+Na^+), 790 (M(^{81}Br)$^+$+1), 788 (M(^{79}Br)$^+$+1); IR (neat): 1738, 1587, 1498, 1455, 1397, 1339, 1273, 1189, 1070, 1008 cm^{-1}; HRMS calcd. for $C_{43}H_{37}N_2O_8{}^{79}BrNa$ [M+Na^+]: 811.1626; Found: 811.1619.

The reaction with 5 mol% catalyst is slow!

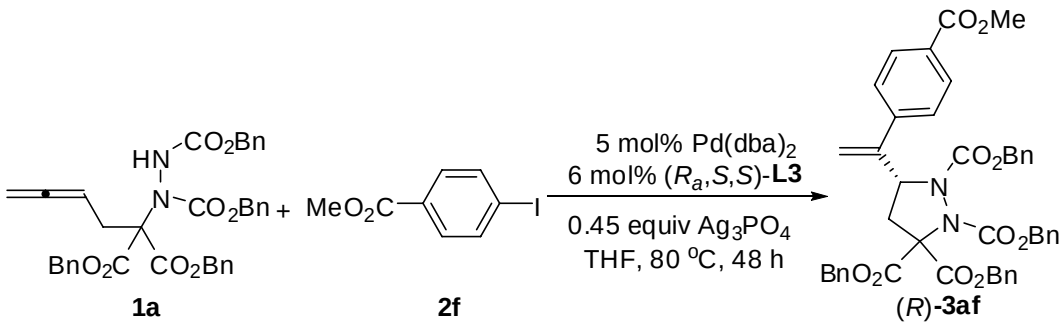
5. 1,2,3,3-Tetrakis(benzyloxycarbonyl)-5-(*R*)-(1'-(4''-acetylphenyl)ethenyl)-pyrazolidine (*R*-3ae)



The reaction of $Pd(dba)_2$ (3 mg, 0.0053 mmol), (R_a,*S*,*S*)-**L3** (4 mg, 0.0063 mmol), Ag_3PO_4 (19 mg, 0.45 mmol), **1a** (64 mg, 0.10 mmol), **2e** (30 mg, 0.12 mmol) afforded

57 mg (75%) of (*R*)-**3ae** as a viscous oil (eluent: petroleum ether : ethyl acetate = 3:1). 95% ee (determined by HPLC analysis (Chiralcel AD-H, hexane/*i*-PrOH = 60/40, 0.7 mL/min, 214 nm), tr 22.9 min (major), 37.1 min (minor)); $[\alpha]^{20}_{D}$ = -20.5 (*c* =1.70, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 2 H), 7.25-7.07 (m, 20 H), 7.01-6.96 (m, 2 H), 5.63 (s, 1 H), 5.45-5.40 (m, 1 H), 5.18 (s, 1 H), 5.11-4.77 (m, 8 H), 3.03 (dd, *J* = 13.6, 8.8 Hz, 1 H), 2.48 (s, 3 H), 2.42 (dd, *J* = 13.6, 2.8 Hz, 1 H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 197.4, 167.6, 165.9, 157.0, 153.2, 143.2, 143.0, 136.2, 135.4, 135.3, 134.8, 134.3, 128.48, 128.45, 128.38, 128.37, 128.22, 128.18, 128.1, 128.0, 127.7, 126.7, 115.7, 72.2, 68.6, 68.3, 68.2, 68.1, 61.0, 41.3, 26.5; MS (ESI): *m/z* 775 ($M+Na^+$), 753 (M^++1); IR (neat): 1738, 1683, 1604, 1560, 1498, 1455, 1402, 1340, 1266, 1187, 1103, 1068, 1013 cm^{-1}; HRMS calcd. for $C_{45}H_{40}N_2O_9Na$ [$M+Na^+$]: 775.2626; Found: 775.2624.

6. 1,2,3,3-Tetrakis(benzyloxycarbonyl)-5-(*R*)-(1'-(4''-methoxylcarbonylphenyl)-ethenyl)pyrazolidine (*R*-3af)

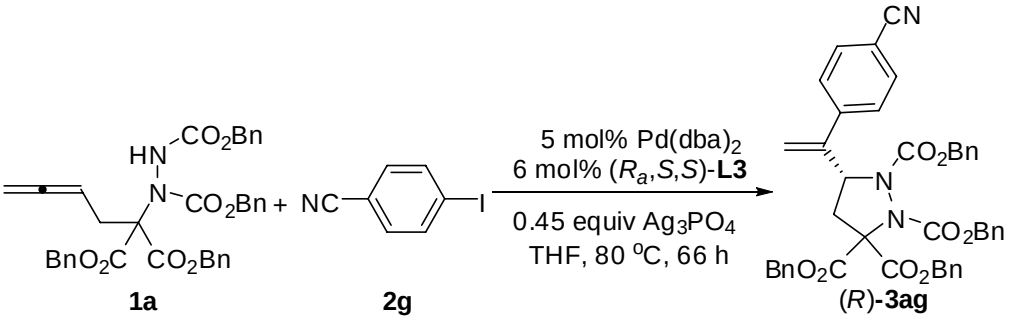


1a **2f** (*R*)-**3af**

The reaction of $Pd(dba)_2$ (3 mg, 0.0053 mmol), (R_a,*S*,*S*)-**L3** (4 mg, 0.0063 mmol), Ag_3PO_4 (19 mg, 0.45 mmol), **1a** (63 mg, 0.10 mmol), **2f** (31 mg, 0.12 mmol) afforded

58 mg (76%) of (*R*)-**3af** as a viscous oil. 93% ee (determined by HPLC analysis (Chiralcel AD-H, hexane/*i*-PrOH = 60/40, 0.7 mL/min, 230 nm), tr 22.4 min (major), 30.5 min (minor)); $[\alpha]^{20}_{D}$ = - 11.1 (*c* = 1.25, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.0 Hz, 2 H), 7.26-7.07 (m, 18 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 7.01-6.97 (m, 2 H), 5.63 (s, 1 H), 5.44-5.39 (m, 1 H), 5.16 (s, 1 H), 5.12-4.76 (m, 8 H), 3.82 (s, 3 H), 3.02 (dd, *J* = 13.6, 8.8 Hz, 1 H), 2.41 (dd, *J* = 13.6, 2.4 Hz, 1 H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 167.6, 166.6, 165.9, 157.0, 153.2, 143.02, 142.97, 135.4, 135.3, 134.8, 134.3, 129.7, 129.3, 128.5, 128.44, 128.42, 128.39, 128.38, 128.2, 128.1, 128.0, 127.7, 126.5, 115.5, 72.2, 68.6, 68.4, 68.3, 68.1, 61.0, 52.1, 41.3; MS (ESI): *m/z* 808 ($M+K^+$), 791 ($M+Na^+$), 769 (M^++1); IR (neat): 1722, 1608, 1498, 1455, 1402, 1342, 1280, 1187, 1112, 1068, 1017 cm^{-1}; HRMS calcd. for $C_{45}H_{40}N_2O_{10}Na$ [$M+Na^+$]: 791.2575; Found: 791.2557.

7. 1,2,3,3-Tetrakis(benzyloxycarbonyl)-5-(*R*)-(1'-(4''-cyanophenyl)ethenyl)-pyrazolidine (*R*-3ag)



The reaction of $Pd(dba)_2$ (3 mg, 0.0053 mmol), (R_a,*S*,*S*)-**L3** (4 mg, 0.0063 mmol), Ag_3PO_4 (19 mg, 0.45 mmol), **1a** (64 mg, 0.10 mmol), **2g** (28 mg, 0.12 mmol)

afforded 58 mg (78%) of (*R*)-**3ag** as a viscous oil. 94% ee (determined by HPLC analysis (Chiralcel AD-H, hexane/*i*-PrOH = 60/40, 0.7 mL/min, 214 nm), tr 24.6 min (major), 43.9 min (minor)); $[\alpha]^{20}{}_{D}$ = - 14.2 (*c* = 1.00, EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (d, *J* = 9.0 Hz, 2 H), 7.29-7.08 (m, 18 H), 7.07-6.95 (m, 4 H), 5.63 (s, 1 H), 5.40-5.33 (m, 1 H), 5.14 (s, 1 H), 5.13-4.90 (m, 5 H), 4.88-4.76 (m, 3 H), 3.02 (dd, *J* = 13.8, 8.7 Hz, 1 H), 2.38 (dd, *J* = 13.8, 2.7 Hz, 1 H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 167.6, 165.9, 156.9, 153.2, 143.1, 142.7, 135.4, 135.2, 134.8, 134.3, 132.2, 128.6, 128.4, 128.30, 128.27, 128.2, 128.0, 127.7, 127.3, 118.5, 116.7, 111.4, 72.2, 68.7, 68.4, 68.3, 68.2, 60.9, 41.2; MS (ESI): *m/z* 774 ($M+K^+$), 758 ($M+Na^+$), 736 (M^++1); IR (neat): 2227, 1738, 1606, 1498, 1455, 1399, 1339, 1275, 1190, 1068, 1003 cm^{-1}; HRMS calcd. for $C_{44}H_{37}N_3O_8Na$ [$M+Na^+$]: 758.2473; Found: 758.2454.

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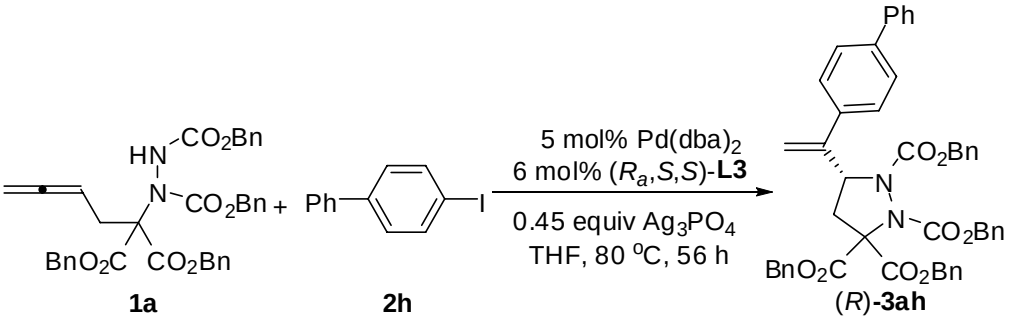
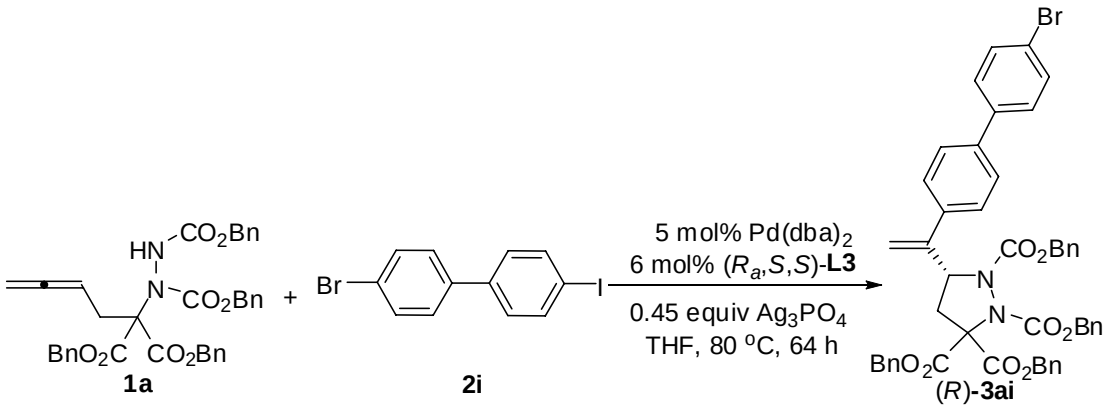
8. 1,2,3,3-Tetrakis(benzyloxycarbonyl)-5-(*R*)-(1'-(4''-phenylphenyl)ethenyl)-pyrazolidine (*R*-3ah)



The reaction of $Pd(dba)_2$ (3 mg, 0.0053 mmol), (R_a,*S*,*S*)-**L3** (4 mg, 0.0063 mmol), Ag_3PO_4 (19 mg, 0.45 mmol), **1a** (64 mg, 0.10 mmol), **2h** (34 mg, 0.12 mmol) afforded 70 mg (88%) of (*R*)-**3ah** as a viscous oil. 92% ee (determined by HPLC

analysis (Chiralcel AD-H, hexane/*i*-PrOH = 60/40, 0.7 mL/min, 230 nm), tr 17.9 min (major), 31.4 min (minor)); $[\alpha]^{20}_{D}$ = - 14.8 (*c* = 1.55, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.45 (m, 2 H), 7.40-7.32 (m, 4 H), 7.28-7.07 (m, 21 H), 7.01-6.97 (m, 2 H), 5.59 (s, 1 H), 5.48-5.44 (m, 1 H), 5.18 (s, 1 H), 5.13-4.79 (m, 8 H), 3.04 (dd, *J* = 13.6, 8.8 Hz, 1 H), 2.54 (dd, *J* = 13.6, 2.4 Hz, 1 H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 167.8, 166.0, 157.0, 153.3, 143.1, 140.6, 140.4, 137.3, 135.5, 135.4, 134.9, 134.4, 128.7, 128.6, 128.43, 128.41, 128.38, 128.36, 128.2, 128.13, 128.09, 128.0, 127.6, 127.4, 127.1, 126.9, 113.7, 72.2, 68.5, 68.3, 68.2, 68.0, 61.2, 41.4; MS (ESI): *m/z* 826 ($M+K^+$), 809 ($M+Na^+$), 786 (M^++1); IR (neat): 1737, 1600, 1586, 1498, 1487, 1455, 1399, 1336, 1272, 1189, 1102, 1069, 1006 cm^{-1}; HRMS calcd. for $C_{49}H_{42}N_2O_8Na$ [$M+Na^+$]: 809.2833; Found: 809.2829.

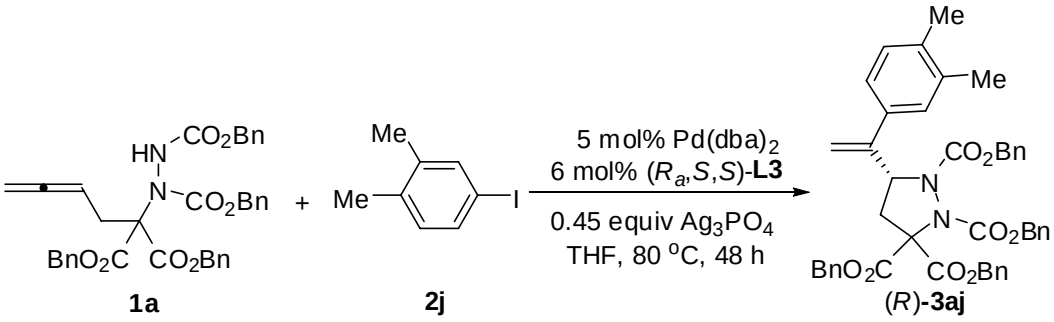
9. 1,2,3,3-Tetrakis(benzyloxycarbonyl)-5-(*R*)-(1'-(4''-(4'''-bromophenyl)phenyl)-ethnyl)pyrazolidine (*R*-3ai)



The reaction of $Pd(dba)_2$ (3 mg, 0.0053 mmol), (R_a,*S*,*S*)-**L3** (4 mg, 0.0063 mmol), Ag_3PO_4 (19 mg, 0.45 mmol), **1a** (64 mg, 0.10 mmol), **2i** (43 mg, 0.12 mmol) afforded

62 mg (71%) of (*R*)-**3ai** as a viscous oil. 92% ee (determined by HPLC analysis (Chiralcel AD-H, hexane/*i*-PrOH = 60/40, 0.7 mL/min, 230 nm), tr 25.5 min (major), 42.0 min (minor)); $[\alpha]^{20}_{D}$ = - 18.7 (*c* = 1.25, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.4 Hz, 2 H), 7.36-7.31 (m, 4 H), 7.24-7.07 (m, 20 H), 7.01-6.97 (m, 2 H), 5.59 (s, 1 H), 5.47-5.42 (m, 1 H), 5.17 (s, 1 H), 5.13-4.79 (m, 8 H), 3.04 (dd, *J* = 13.6, 8.8 Hz, 1 H), 2.52 (dd, *J* = 13.6, 2.8 Hz, 1 H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 167.7, 166.0, 157.1, 153.3, 143.1, 139.33, 139.28, 137.8, 135.5, 135.4, 134.9, 134.4, 131.9, 128.5, 128.44, 128.42, 128.37, 128.20, 128.18, 128.15, 128.1, 128.0, 127.6, 127.1, 126.9, 121.7, 114.0, 72.2, 68.5, 68.3, 68.2, 68.1, 61.2, 41.4; MS (ESI): *m/z* 889 ($M(^{81}Br)+Na^+$), 887 ($M(^{79}Br)+Na^+$); IR (neat): 1738, 1587, 1498, 1483, 1455, 1392, 1340, 1275, 1186, 1070, 1002 cm^{-1}; HRMS calcd. for $C_{49}H_{41}N_2O_8{}^{79}BrNa$ [$M+Na^+$]: 887.1939; Found: 887.1941.

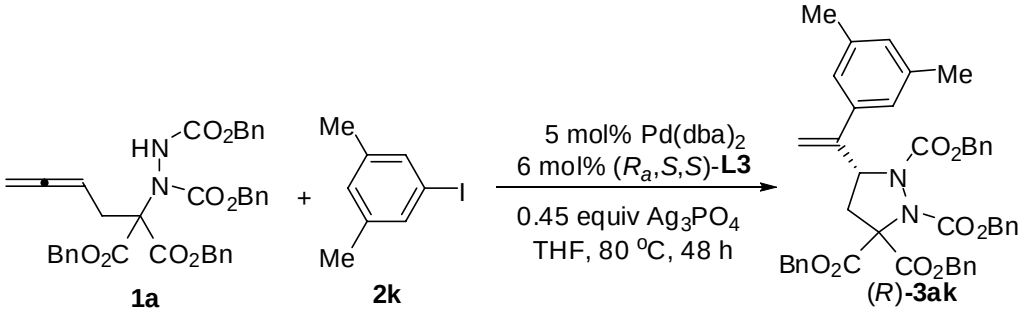
10. 1,2,3,3-Tetrakis(benzyloxycarbonyl)-5-(*R*)-(1'-(3",4"-dimethylphenyl)-ethenylpyrazolidine (*R*-3aj)



The reaction of $Pd(dba)_2$ (3 mg, 0.0053 mmol), (R_a,*S*,*S*)-**L3** (4 mg, 0.0063 mmol), Ag_3PO_4 (19 mg, 0.45 mmol), **1a** (63 mg, 0.10 mmol), **2j** (28 mg, 0.12 mmol) afforded

56 mg (76%) of (*R*)-**3aj** as a viscous oil. 95% ee (determined by HPLC analysis (Chiralcel OD-H, hexane/*i*-PrOH = 60/40, 0.5 mL/min, 230 nm), tr 15.9 min (major), 18.8 min (minor)); $[\alpha]^{20}_{D}$ = - 11.6 (*c* = 1.20, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.07 (m, 18 H), 7.01-6.97 (m, 2 H), 6.93 (d, *J* = 7.6 Hz, 1 H), 6.85 (s, 1 H), 6.78 (d, *J* = 7.6 Hz, 1 H), 5.50 (s, 1 H), 5.43-5.37 (m, 1 H), 5.12-4.77 (m, 9 H), 3.00 (dd, *J* = 13.6, 8.8 Hz, 1 H), 2.50 (dd, *J* = 13.6, 2.8 Hz, 1 H), 2.14 (s, 3 H), 2.10 (s, 3 H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 167.8, 166.0, 157.1, 153.3, 143.5, 136.6, 136.3, 136.0, 135.6, 135.4, 134.9, 134.5, 129.7, 128.43, 128.38, 128.35, 128.27, 128.2, 128.14, 128.10, 128.06, 128.0, 127.7, 127.6, 124.0, 112.7, 72.2, 68.5, 68.3, 68.1, 68.0, 61.3, 41.5, 19.8, 19.4; MS (ESI): *m/z* 777 ($M+K^+$), 761 ($M+Na^+$); IR (neat): 1740, 1608, 1586, 1499, 1455, 1399, 1337, 1274, 1188, 1069, 1003 cm^{-1}; HRMS calcd. for $C_{45}H_{42}N_2O_8Na$ [$M+Na^+$]: 761.2833; Found: 761.2821.

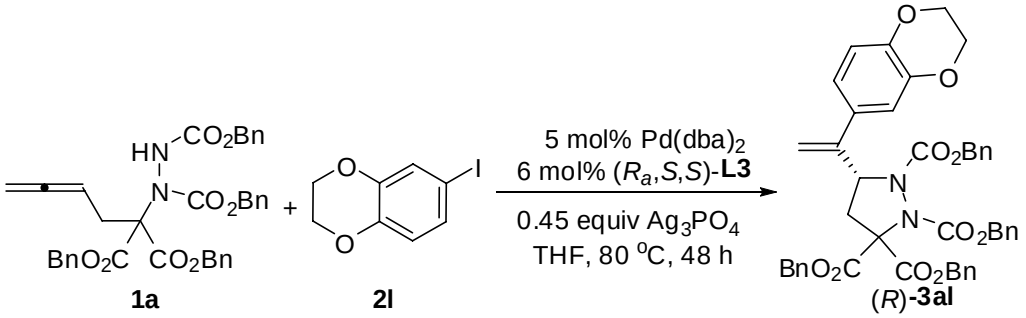
11. 1,2,3,3-Tetrakis(benzyloxycarbonyl)-5-(*R*)-(1'-(3",5"-dimethylphenyl)-ethenylpyrazolidine (*R*-3ak)



The reaction of $Pd(dba)_2$ (3 mg, 0.0053 mmol), (R_a,*S*,*S*)-**L3** (4 mg, 0.0063 mmol), Ag_3PO_4 (19 mg, 0.45 mmol), **1a** (64 mg, 0.10 mmol), **2k** (28 mg, 0.12 mmol)

afforded 62 mg (83%) of (*R*)-**3ak** as a viscous oil. 93% ee (determined by HPLC analysis (Chiralcel OD-H, hexane/*i*-PrOH = 60/40, 0.5 mL/min, 230 nm), tr 8.2 min (major), 9.6 min (minor)); $[\alpha]^{20}{}_{D}$ = - 4.1 (*c* = 1.35, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.07 (m, 18 H), 7.02-6.97 (m, 2 H), 6.81 (s, 1 H), 6.68 (s, 2 H), 5.52 (s, 1 H), 5.43-5.38 (m, 1 H), 5.13-4.78 (m, 9 H), 3.01 (dd, *J* = 13.6, 8.8 Hz, 1 H), 2.49 (dd, *J* = 13.6, 2.8 Hz, 1 H), 2.16 (s, 6 H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 167.8, 166.0, 157.1, 153.3, 143.8, 138.5, 137.9, 135.6, 135.4, 134.9, 134.5, 129.5, 128.42, 128.38, 128.35, 128.21, 128.18, 128.14, 128.11, 128.06, 128.0, 127.6, 124.4, 113.2, 72.2, 68.4, 68.3, 68.2, 68.0, 61.3, 41.5, 21.3; MS (ESI): *m/z* 777 ($M+K^+$), 761 ($M+Na^+$), 739 (M^++1); IR (neat): 1740, 1599, 1498, 1455, 1397, 1338, 1275, 1188, 1070, 1003 cm^{-1}; HRMS calcd. for $C_{45}H_{42}N_2O_8Na$ [$M+Na^+$]: 761.2833; Found: 761.2818.

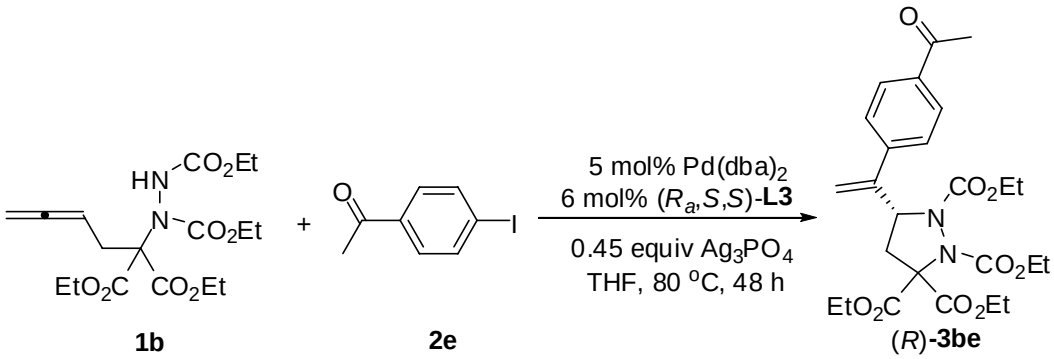
12. 1,2,3,3-Tetrakis(benzyloxycarbonyl)-5-(*R*)-(1'-(2''-(2'',3''-dihydrobenzo-[*b*][1'',4'']dioxin-6''-yl))ethenyl-pyrazolidine (*R*-3al)



The reaction of $Pd(dba)_2$ (3 mg, 0.0053 mmol), (R_a,*S*,*S*)-**L3** (4 mg, 0.0063 mmol), Ag_3PO_4 (19 mg, 0.45 mmol), **1a** (66 mg, 0.10 mmol), **2l** (31 mg, 0.12 mmol) afforded

59 mg (74%) of (*R*)-**3al** as a viscous oil. 93% ee (determined by HPLC analysis (Chiralcel AD-H, hexane/*i*-PrOH = 60/40, 0.7 mL/min, 230 nm), tr 19.7 min (major), 25.0 min (minor)); $[\alpha]^{20}_{D}$ = - 14.9 (*c* = 1.20, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.07 (m, 18 H), 7.03-6.98 (m, 2 H), 6.67-6.62 (m, 2 H), 6.53-6.50 (m, 1 H), 5.47 (s, 1 H), 5.36-5.31 (m, 1 H), 5.11-4.79 (m, 9 H), 4.13 (s, 4 H), 2.99 (dd, *J* = 13.2, 8.4 Hz, 1 H), 2.52 (dd, *J* = 13.2, 2.0 Hz, 1 H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 167.8, 166.0, 157.0, 153.3, 143.3, 142.7, 135.6, 135.4, 134.9, 134.5, 131.9, 128.42, 128.39, 128.37, 128.3, 128.2, 128.12, 128.09, 128.06, 128.0, 127.6, 119.7, 117.1, 115.4, 112.6, 72.2, 68.5, 68.24, 68.17, 68.0, 64.3, 64.2, 61.2, 41.4; MS (ESI): *m/z* 807 ($M+K^+$), 791 ($M+Na^+$), 769 (M^++1); IR (neat): 1739, 1609, 1579, 1508, 1455, 1398, 1284, 1248, 1188, 1067, 1003 cm^{-1}; HRMS calcd. for $C_{45}H_{40}N_2O_{10}Na$ [$M+Na^+$]: 791.2575; Found: 791.2551.

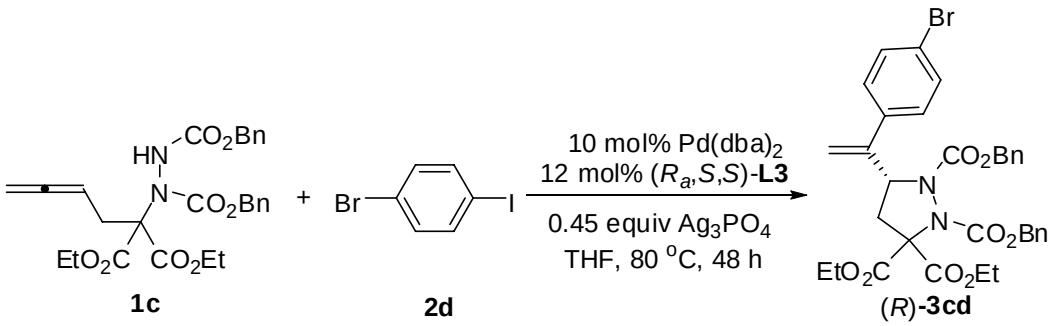
13. 1,2,3,3-Tetrakis(ethoxycarbonyl)-5-(*R*)-(1'-(4''-acetylphenyl)ethenyl)-pyrazolidine (*R*-3be)



The reaction of $Pd(dba)_2$ (3 mg, 0.0053 mmol), (R_a,*S*,*S*)-**L3** (4 mg, 0.0063 mmol), Ag_3PO_4 (19 mg, 0.45 mmol), **1b** (38 mg, 0.098 mmol), **2e** (30 mg, 0.12 mmol)

afforded 41 mg (83%) of (*R*)-**3be** as a viscous oil (eluent: petroleum ether : ethyl acetate = 2:1). 93% ee (determined by HPLC analysis (Chiralcel OD-H, hexane/*i*-PrOH = 60/40, 0.7 mL/min, 214 nm), tr 6.4 min (major), 8.1 min (minor)); $[\alpha]^{20}_{D}$ = - 34.8 (*c* = 1.35, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 5.78 (s, 1 H), 5.46-5.41 (m, 2 H), 4.32-3.98 (m, 6 H), 4.14 (q, *J* = 6.8 Hz, 2 H), 3.07 (dd, *J* = 13.2, 8.4 Hz, 1 H), 2.60 (s, 3 H), 2.49 (dd, *J* = 13.2, 3.2 Hz, 1 H), 1.33-1.22 (m, 9 H), 1.19 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 197.5, 168.0, 166.1, 157.1, 153.5, 143.8, 143.5, 136.4, 128.6, 126.9, 115.4, 72.1, 63.1, 62.6, 62.5, 60.9, 41.5, 26.6, 14.4, 13.9, 13.7; MS (ESI): *m/z* 527 ($M+Na^+$), 505 (M^++1); IR (neat): 1745, 1685, 1604, 1568, 1467, 1405, 1377, 1337, 1267, 1192, 1072, 1038 cm^{-1}; HRMS calcd. for $C_{25}H_{32}N_2O_9Na$ [$M+Na^+$]: 527.2000; Found: 527.2007.

14. 1,2-Bis(benzyloxycarbonyl)-3,3-bis(ethoxycarbonyl)-5-(*R*)-(1'-(4''-bromo-phenyl)ethenyl) pyrazolidine (*R*-3cd)

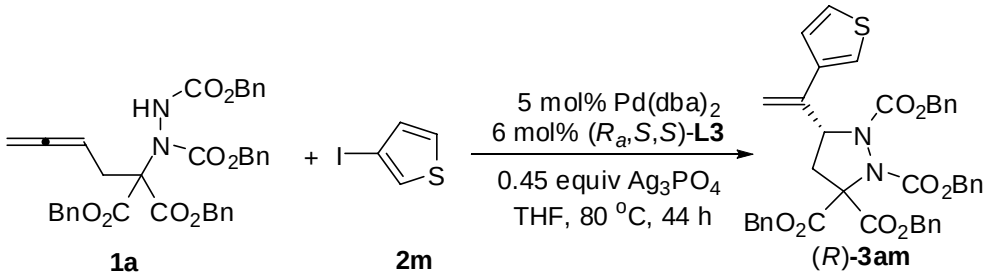


The reaction of $Pd(dba)_2$ (6 mg, 0.011 mmol), (R_a,*S*,*S*)-**L3** (8 mg, 0.013 mmol), Ag_3PO_4 (19 mg, 0.45 mmol), **1c** (51 mg, 0.10 mmol), **2d** (34 mg, 0.12 mmol)

afforded 57 mg (86%) of (*R*)-**3cd** as a viscous oil. 95% ee (determined by HPLC analysis (Chiralcel OD-H, hexane/*i*-PrOH = 85/15, 0.7 mL/min, 230 nm), tr 9.6 min (major), 16.4 min (minor)); $[\alpha]^{20}_{D}$ = -9.1 (*c* =1.20, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.0 Hz, 2 H), 7.35-7.26 (m, 10 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 5.66 (s, 1 H), 5.44-5.39 (m, 1 H), 5.30 (s, 1 H), 5.28-5.16 (m, 3 H), 5.07 (d, *J* = 12.4 Hz, 1 H), 4.17-4.09 (m, 1 H), 4.08-3.99 (m, 3 H), 3.07 (dd, *J* = 13.6, 8.8 Hz, 1 H), 2.52 (dd, *J* = 13.6, 3.2 Hz, 1 H), 1.111 (t, *J* = 6.8 Hz, 3 H), 1.107 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 167.9, 166.0, 156.9, 153.3, 143.2, 137.6, 135.5, 135.4, 131.6, 128.44, 128.35, 128.3, 128.2, 128.1, 127.6, 121.9, 114.4, 72.2, 68.6, 68.3, 62.5, 61.1, 41.3, 13.7, 13.6; MS (ESI): *m/z* 689 (M(^{81}Br)+Na^+), 687 (M(^{79}Br)+Na^+), 667 (M^+(^{81}Br)+1), 665 (M^+(^{79}Br)+1); IR (neat): 1738, 1587, 1489, 1455, 1394, 1338, 1273, 1196, 1072, 1009 cm^{-1}; HRMS calcd. for $C_{33}H_{33}N_2O_8{}^{79}BrNa$ [M+Na^+]: 687.1313; Found: 687.1309.

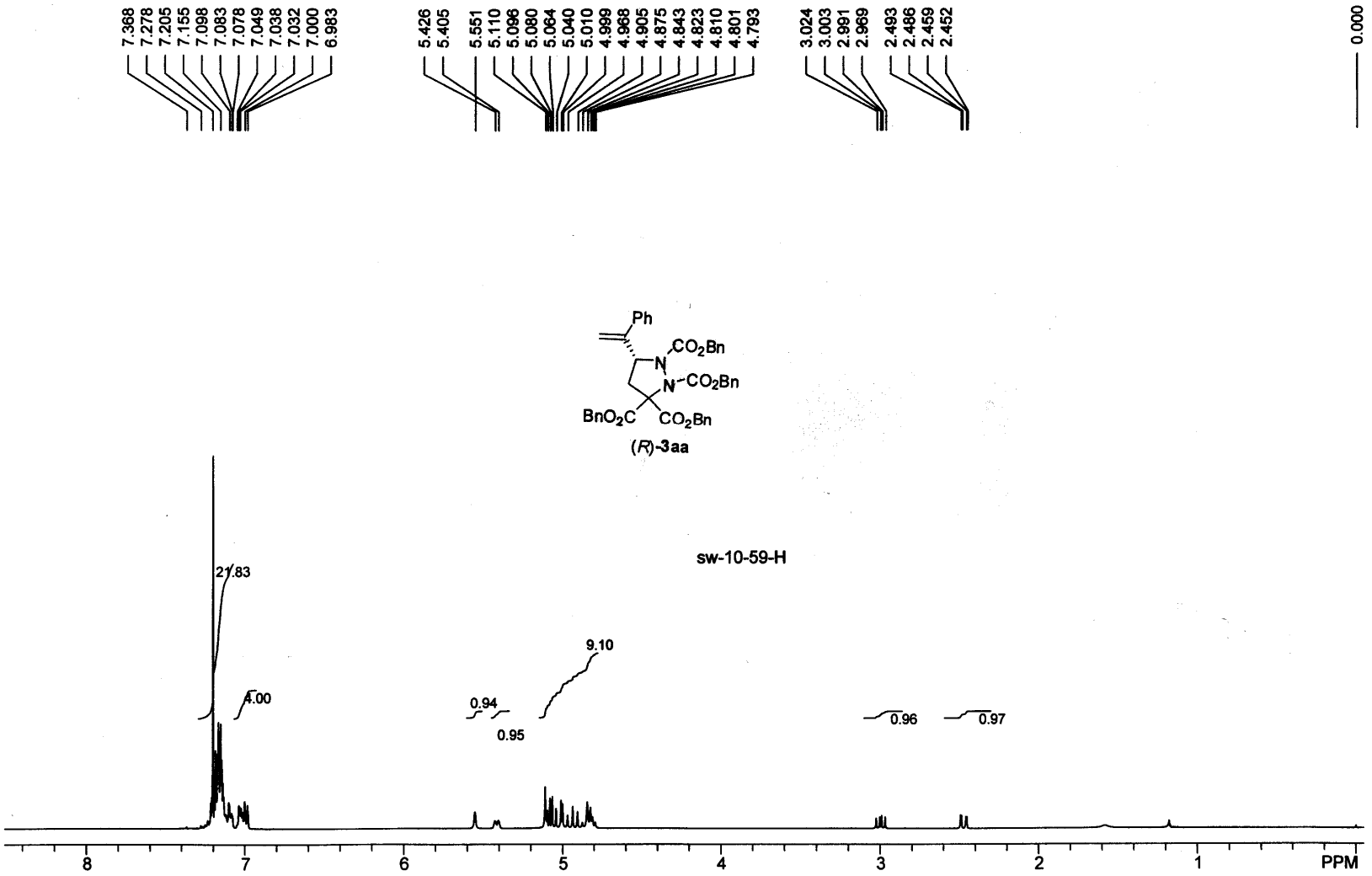
The reaction with 5 mol% catalyst is slow!

15. 1,2,3,3-Tetrakis(benzyloxycarbonyl)-5-(*R*)-(1'-(3"-thienyl)ethenyl)-pyrazolidine (*R*-3am)



The reaction of $Pd(dba)_2$ (3 mg, 0.0053 mmol), (R_a,*S*,*S*)-**L3** (4 mg, 0.0063 mmol),

Ag_3PO_4 (19 mg, 0.45 mmol), **1a** (66 mg, 0.10 mmol), **2m** (26 mg, 0.12 mmol) afforded 63 mg (85%) of (*R*)-**3am** as a viscous oil. 92% ee (determined by HPLC analysis (Chiralcel OD-H, hexane/*i*-PrOH = 60/40, 0.7 mL/min, 214 nm), tr 8.4 min (major), 13.7 min (minor)); $[\alpha]^{20}_{D}$ = + 7.2 (*c* = 1.00, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.09 (m, 19 H), 7.00-6.95 (m, 2 H), 6.91 (dd, *J* = 5.2, 1.4 Hz, 1 H), 6.85 (bs, 1 H), 5.50 (s, 1 H), 5.30-5.25 (m, 1 H), 5.17 (s, 1 H), 5.12-4.78 (m, 8 H), 3.11 (dd, *J* = 13.6, 8.8 Hz, 1 H), 2.60 (dd, *J* = 13.6, 2.8 Hz, 1 H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 167.7, 165.9, 156.9, 153.2, 139.3, 138.6, 135.5, 135.3, 134.9, 134.4, 128.43, 128.41, 128.36, 128.3, 128.22, 128.18, 128.14, 128.09, 128.0, 127.6, 126.0, 125.8, 120.7, 112.3, 72.3, 68.5, 68.3, 68.2, 68.1, 61.2, 41.7; MS (ESI): *m/z* 755 ($M+K^+$), 739 ($M+Na^+$), 717 (M^++1); IR (neat): 1738, 1632, 1586, 1498, 1455, 1399, 1340, 1278, 1187, 1069, 1003 cm^{-1}; HRMS calcd. for $C_{41}H_{36}N_2O_8SNa$ [$M+Na^+$]: 739.2085; Found: 739.2070.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7.083
7.078
7.049
7.038
7.032
7.000
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5.426
5.405
5.551
5.110
5.096
5.080
5.064
5.040
5.010
4.999
4.968
4.905
4.875
4.843
4.823
4.810
4.801
4.793
3.024
3.003
2.991
2.969
2.493
2.486
2.459
2.452
0.000
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N
CO2Bn
BnO2C
CO2Bn
(R)-3aa
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0.96
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7
6
5
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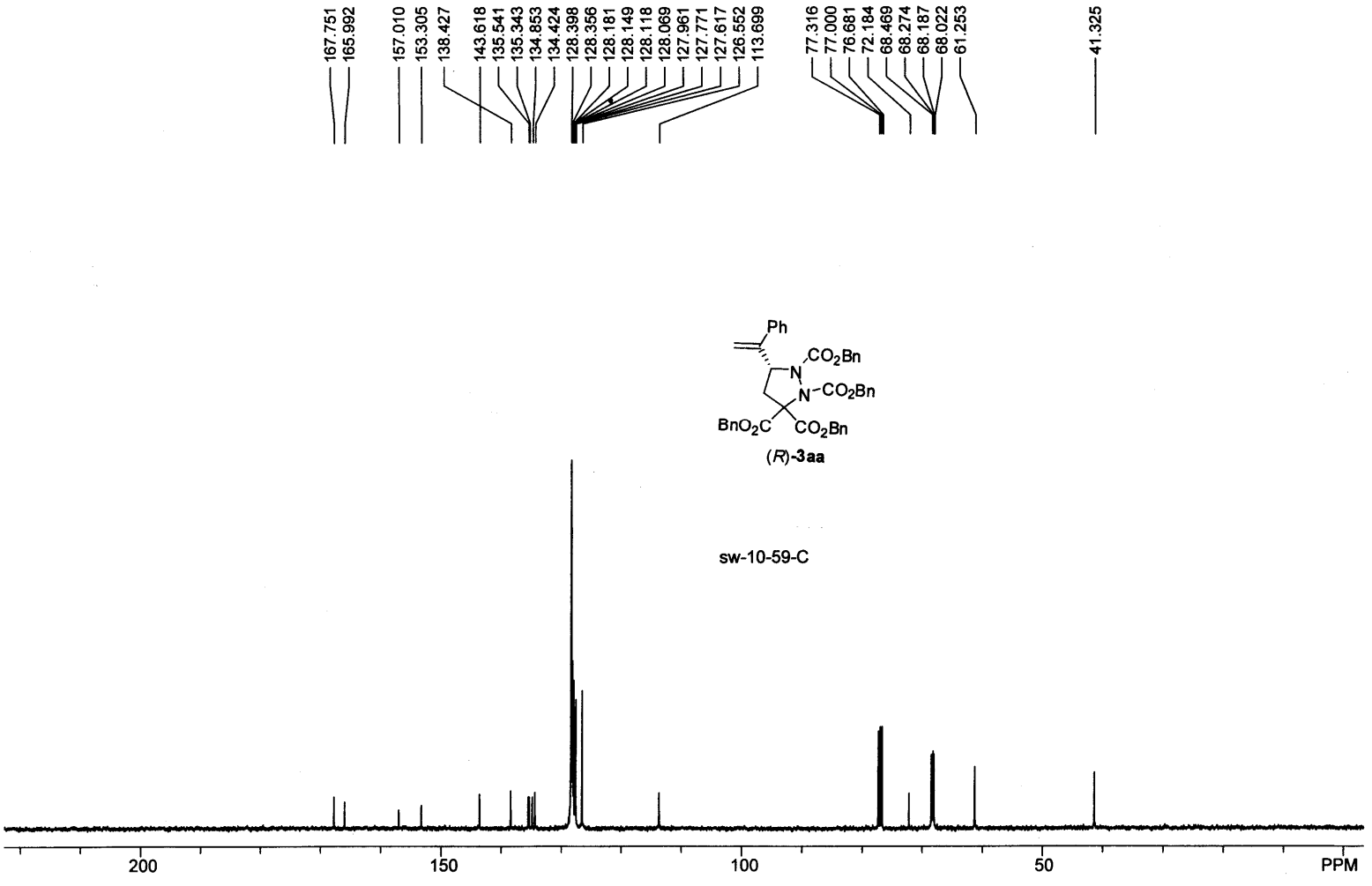
3
2
1
PPM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128.149
128.118
128.069
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127.617
126.552
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72.184
68.469
68.274
68.187
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61.253
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sw-10-59-C
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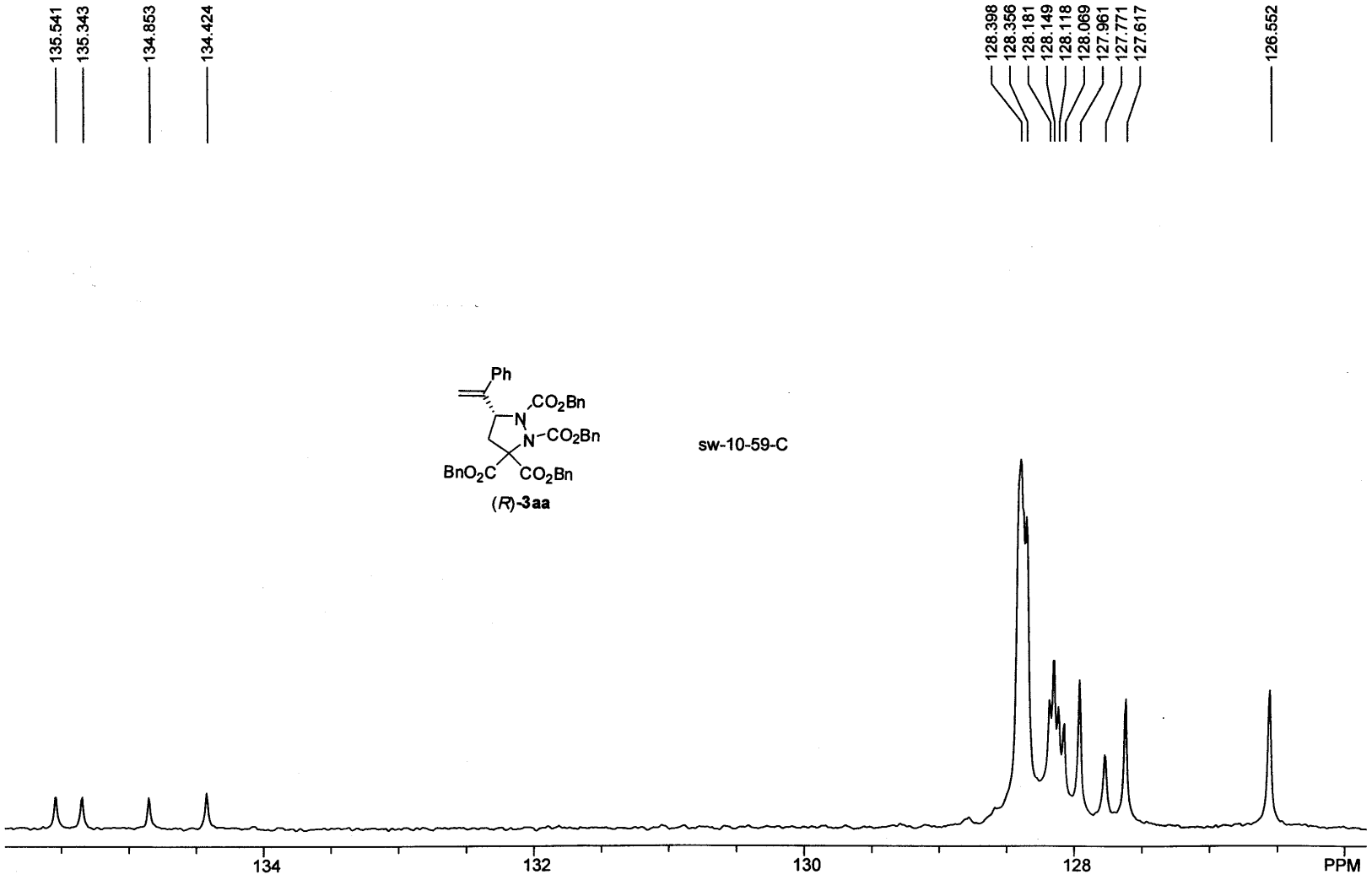
150
100
50
PPM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Ph
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CO2Bn
(R)-3aa
sw-10-59-C
134
132
130
128
PPM

HPLC REPORT

Sample Name:sw-3-62rac ad250 80 0.8.che
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Method:
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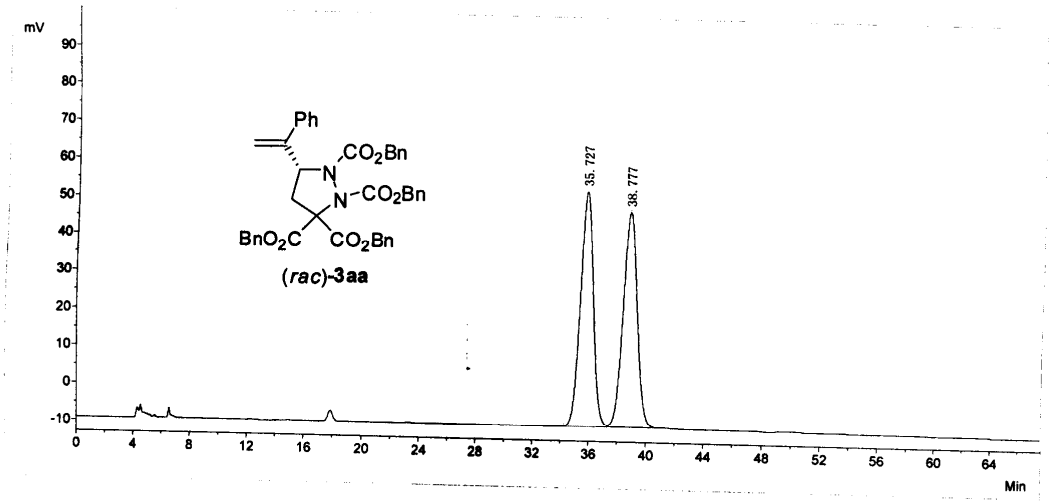
the detection wavelength: 230



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Total			119864.2	7799111.9	100.0000

HPLC REPORT

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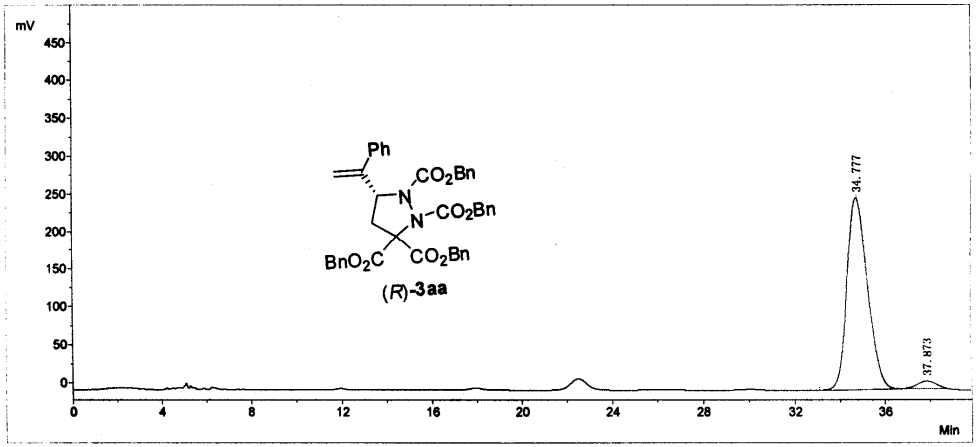
Time:10:36
Method:
column:
the mobile phase:
Velocity:
the detection wavelength:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
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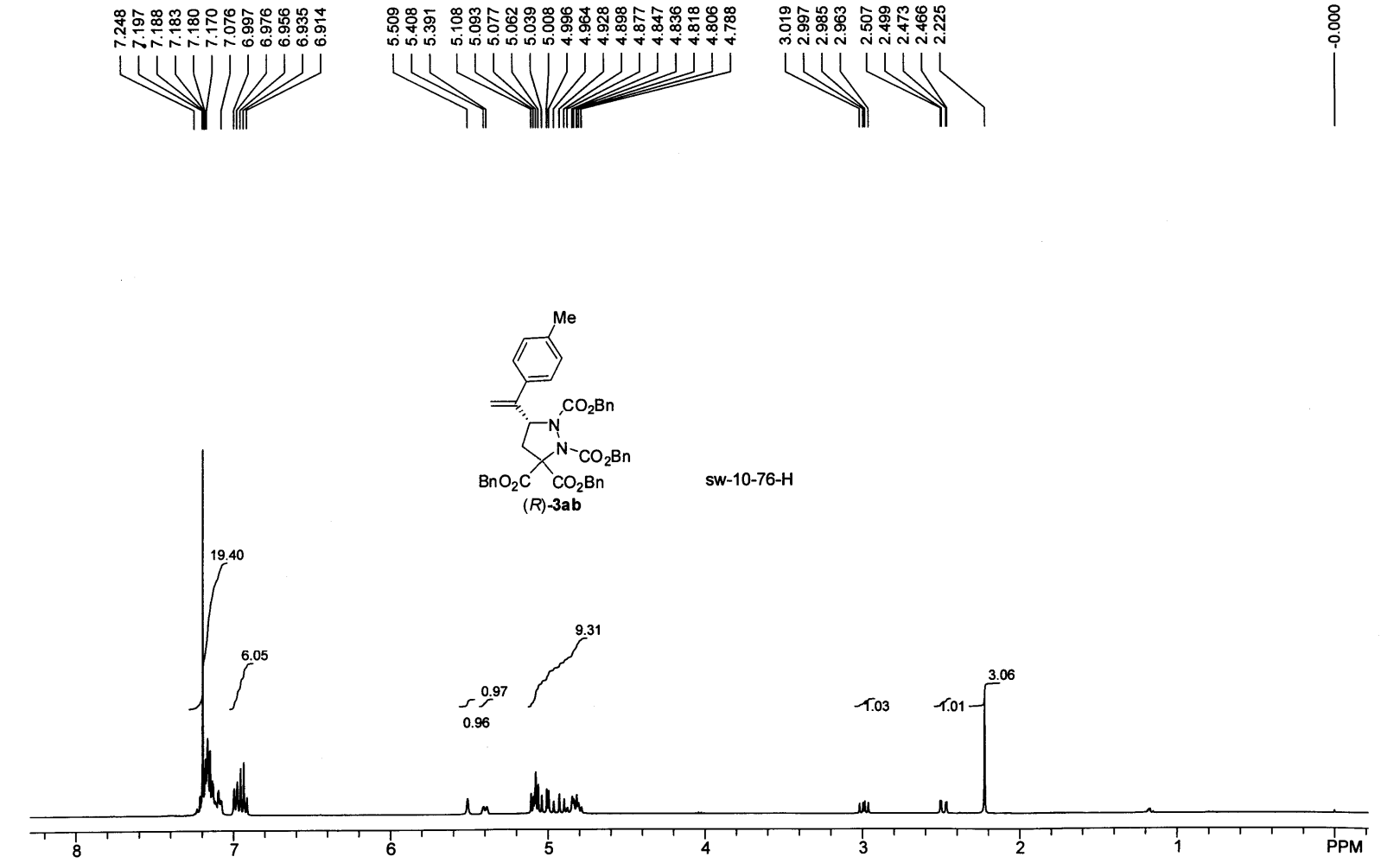
Total			263358.0	16577337.8	100.0000

ee 93.3%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5.408
5.391
5.108
5.093
5.077
5.062
5.039
5.008
4.996
4.964
4.928
4.898
4.877
4.847
4.836
4.818
4.806
4.788
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2.507
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2.473
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N
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CO2Bn
(R)-3ab
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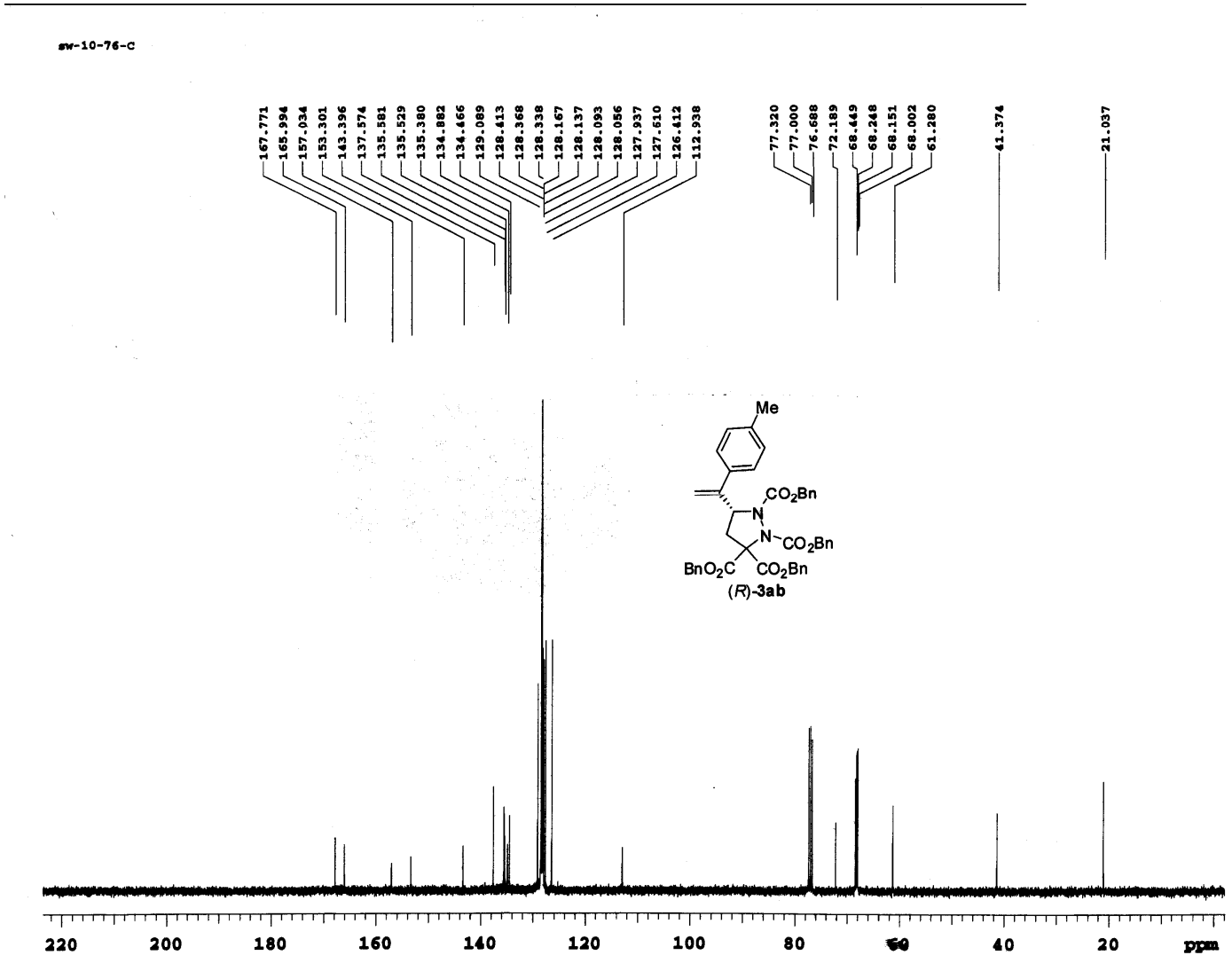
PPM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135.380
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134.466
129.089
128.413
128.368
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128.167
128.137
128.093
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68.248
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41.374
21.037
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N
N
CO2Bn
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140
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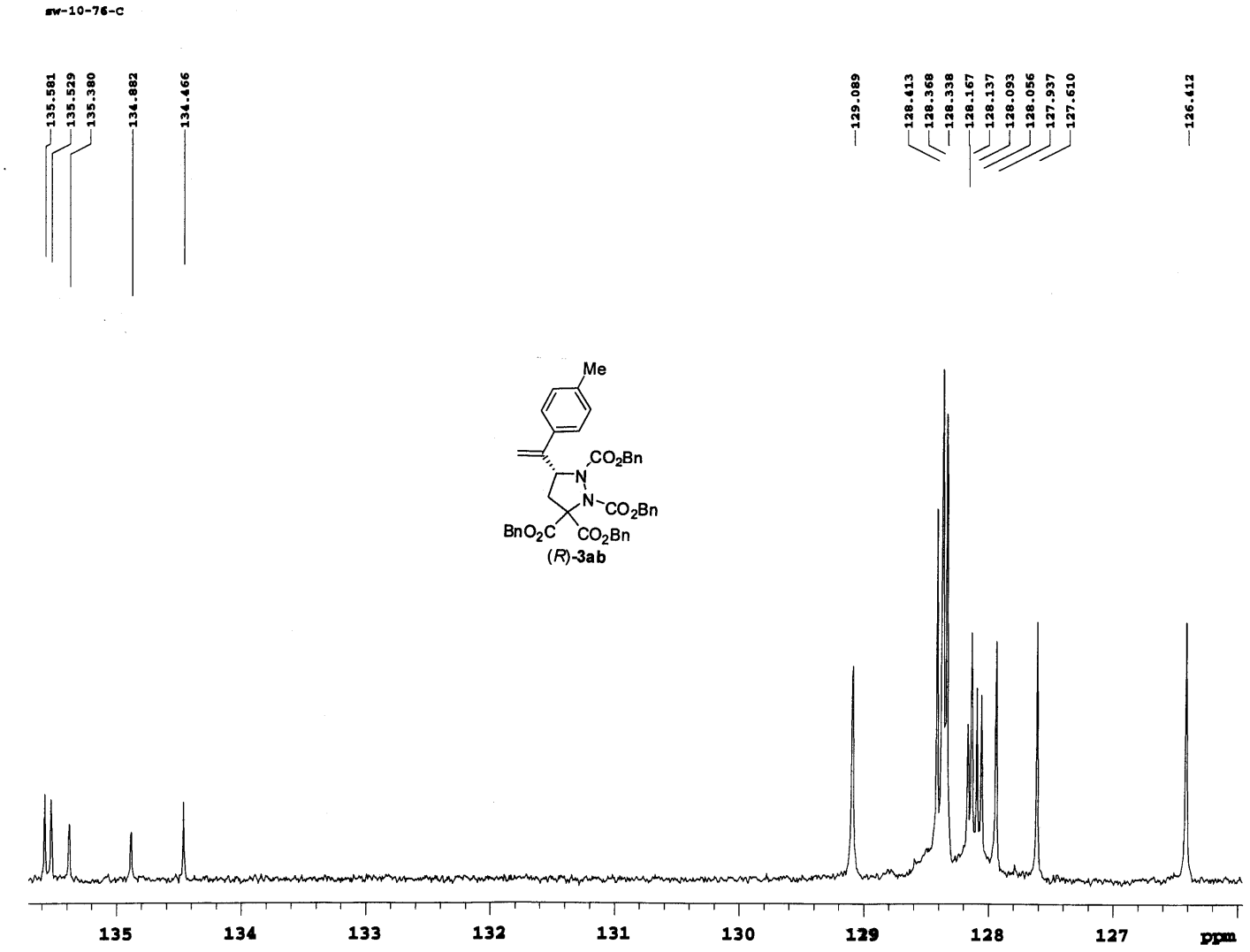
20
ppm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127.937
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N
CO2Bn
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CO2Bn
(R)-3ab
135
134
133
132
131
130
129
128
127
ppm

HPLC REPORT

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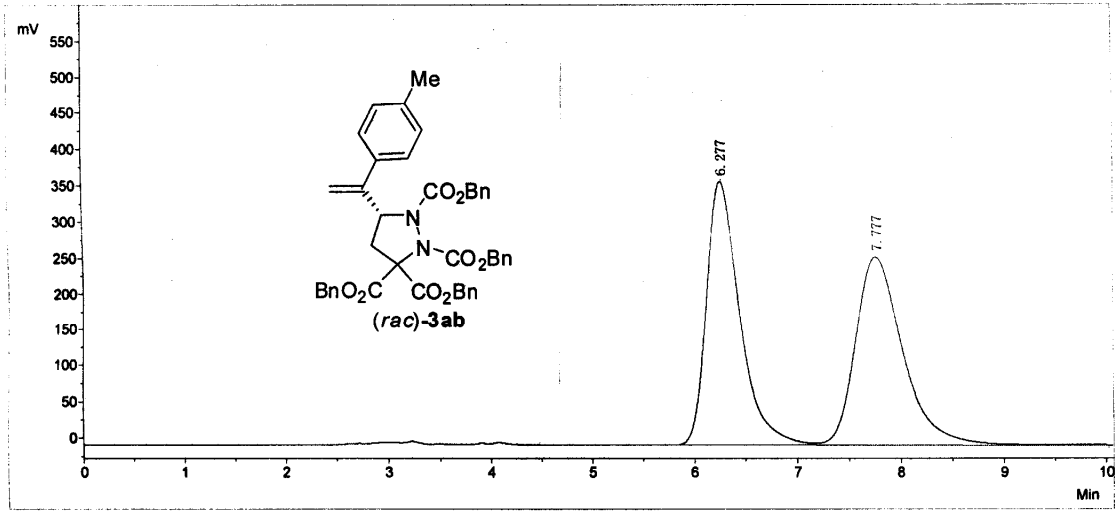

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HPLC REPORT

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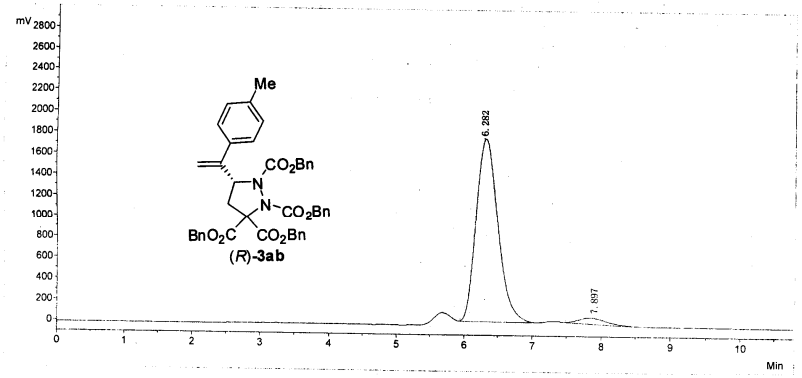
column:
Velocity:

Date: 2008-12-31
Method:
the mobile phase:
the detection wavelength:



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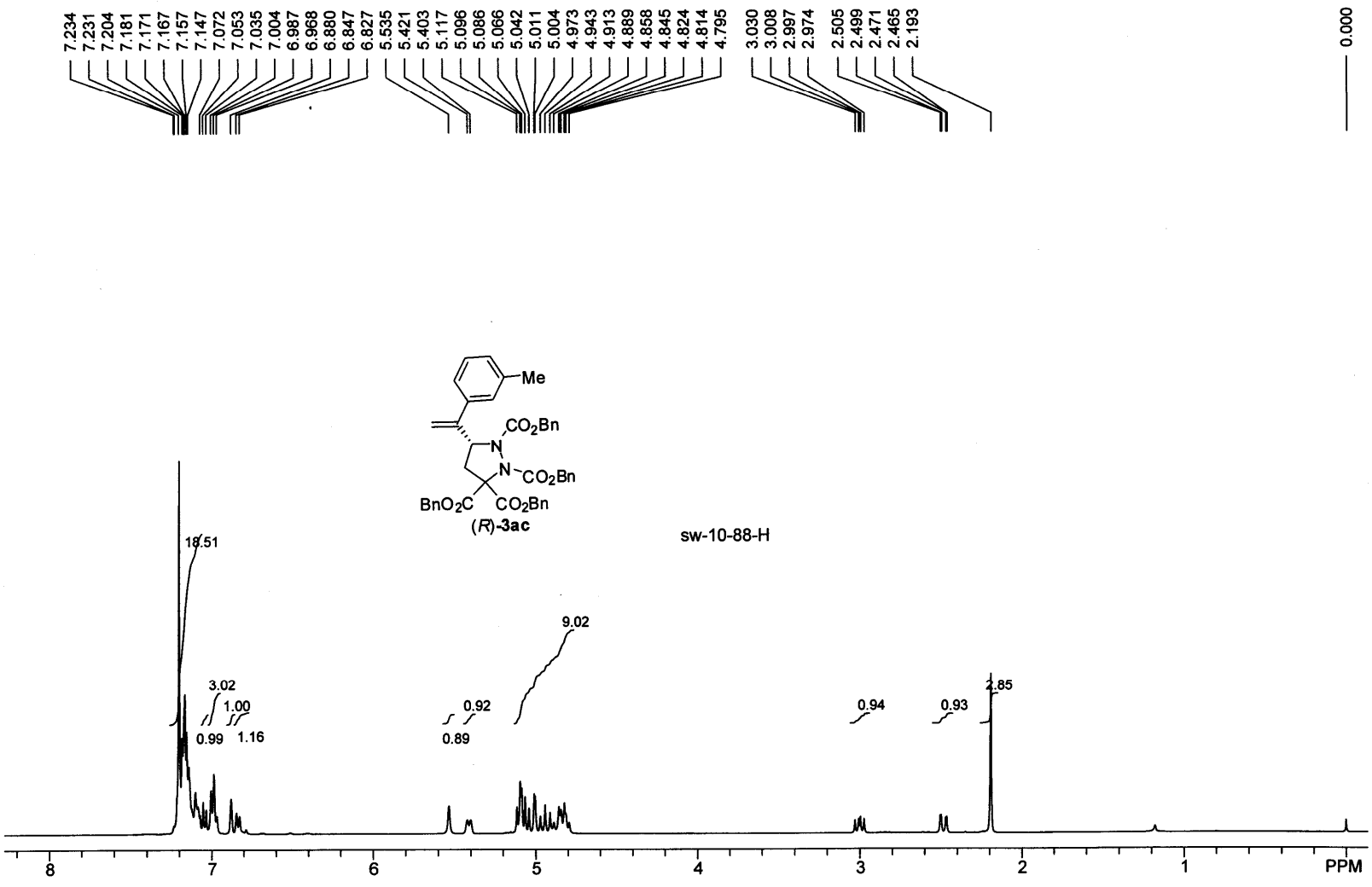
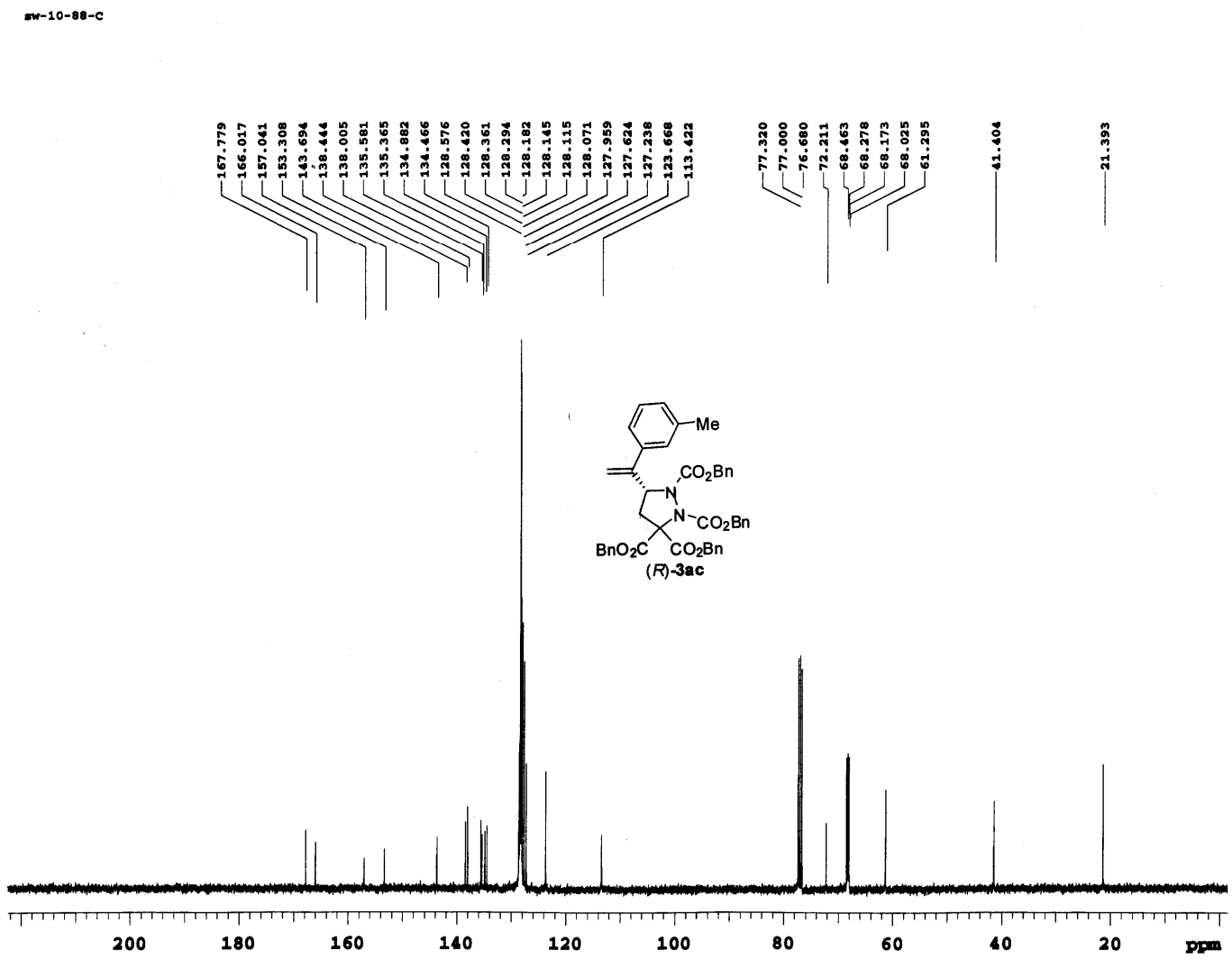
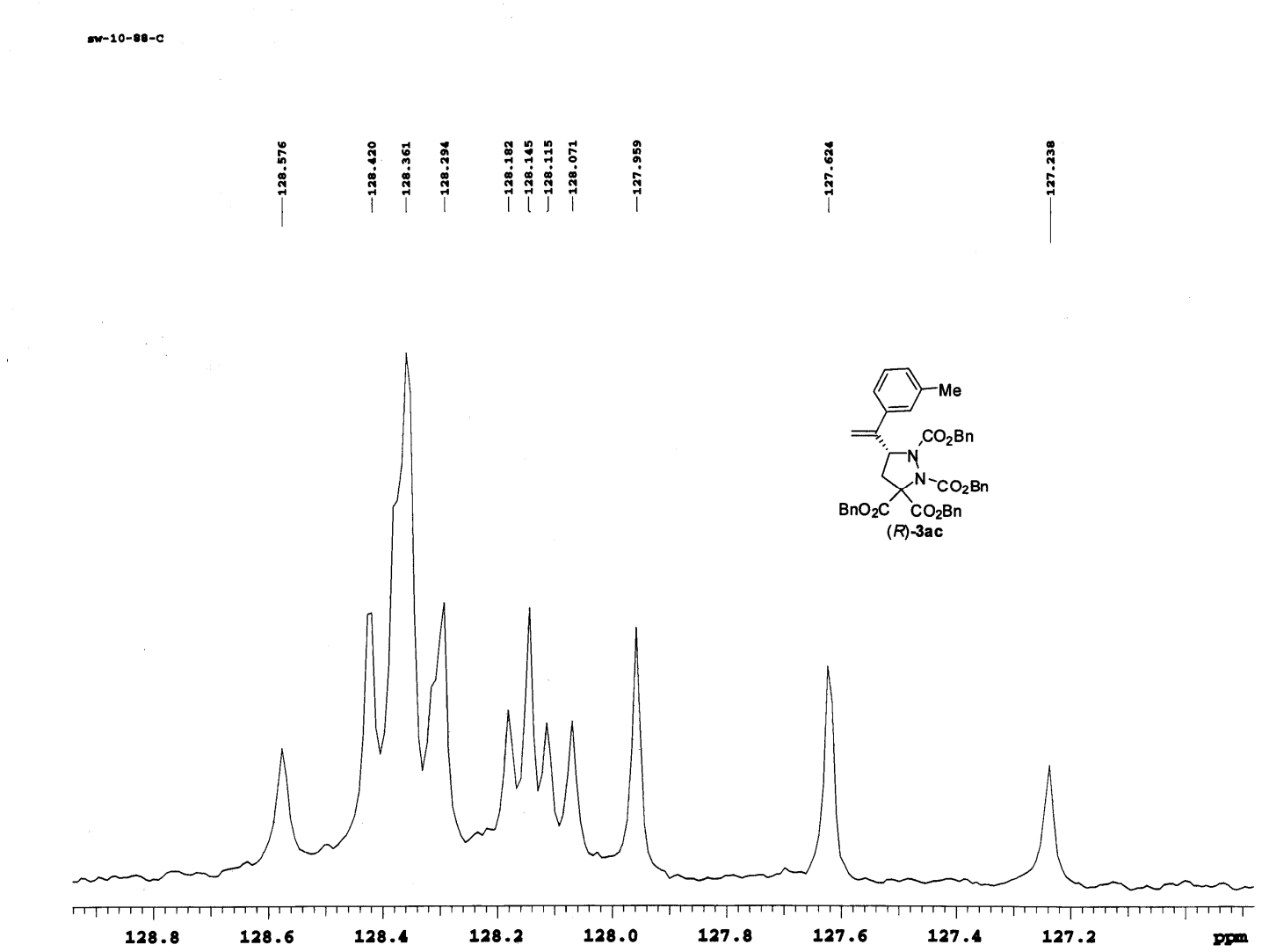
2	2	7.897	56509.7	1509093.8	3.7464
Total			1782231.2	40281366.4	100.0000

ee = 96.2536 - 3.7464
= 92.5%


7.234
7.231
7.204
7.181
7.171
7.167
7.157
7.147
7.072
7.053
7.035
7.004
6.987
6.968
6.880
6.847
6.827
5.535
5.421
5.403
5.117
5.096
5.086
5.066
5.042
5.011
5.004
4.973
4.943
4.913
4.889
4.858
4.845
4.824
4.814
4.795
3.030
3.008
2.997
2.974
2.505
2.499
2.471
2.465
2.193
0.000
Me
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ac
sw-10-88-H
18.51
3.02
1.00
0.99
1.16
0.92
0.89
9.02
0.94
0.93
2.85
8
7
6
5
4
3
2
1
PPM

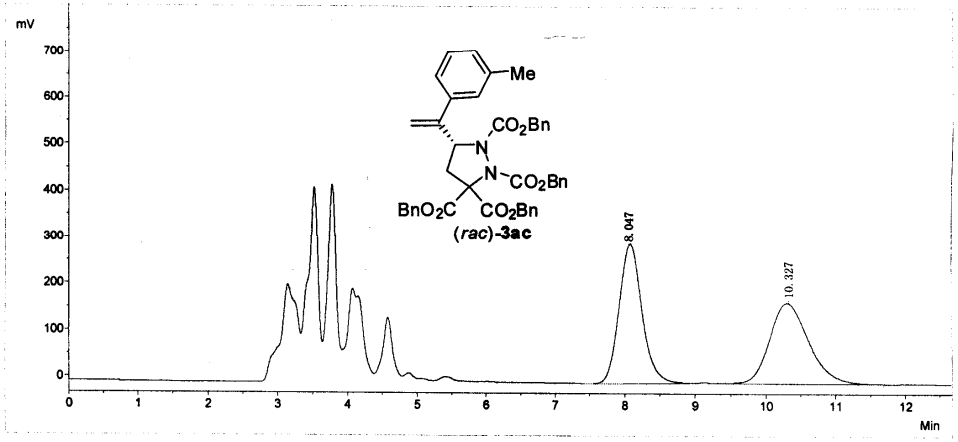

sw-10-08-C
167.779
166.017
157.041
153.308
143.694
138.444
138.005
135.581
135.365
134.882
134.466
128.576
128.420
128.361
128.294
128.182
128.145
128.115
128.071
127.959
127.624
127.238
123.668
113.422
77.320
77.000
76.680
72.211
68.463
68.278
68.173
68.025
61.295
41.404
21.393
Me
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ac
200
180
160
140
120
100
80
60
40
20
ppm


sw-10-88-C
128.576
128.420
128.361
128.294
128.182
128.145
128.115
128.071
127.959
127.624
127.238
Me
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ac
128.8
128.6
128.4
128.2
128.0
127.8
127.6
127.4
127.2
ppm

HPLC REPORT

Sample Name:sw-3-74rac od 80.che
Time:15:29
column: ODH
Velocity: 0.7

Date:2009-04-15
Method:
the mobile phase: 8%
the detection wavelength:214

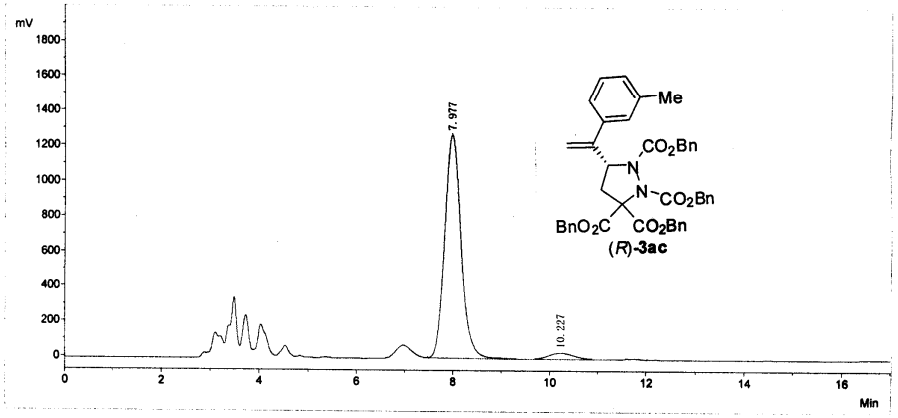


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	8.047	293015.7	6743191.0	50.1333
2	2	10.327	172038.8	6707320.0	49.8667
Total			465054.5	13450511.0	100.0000

HPLC REPORT

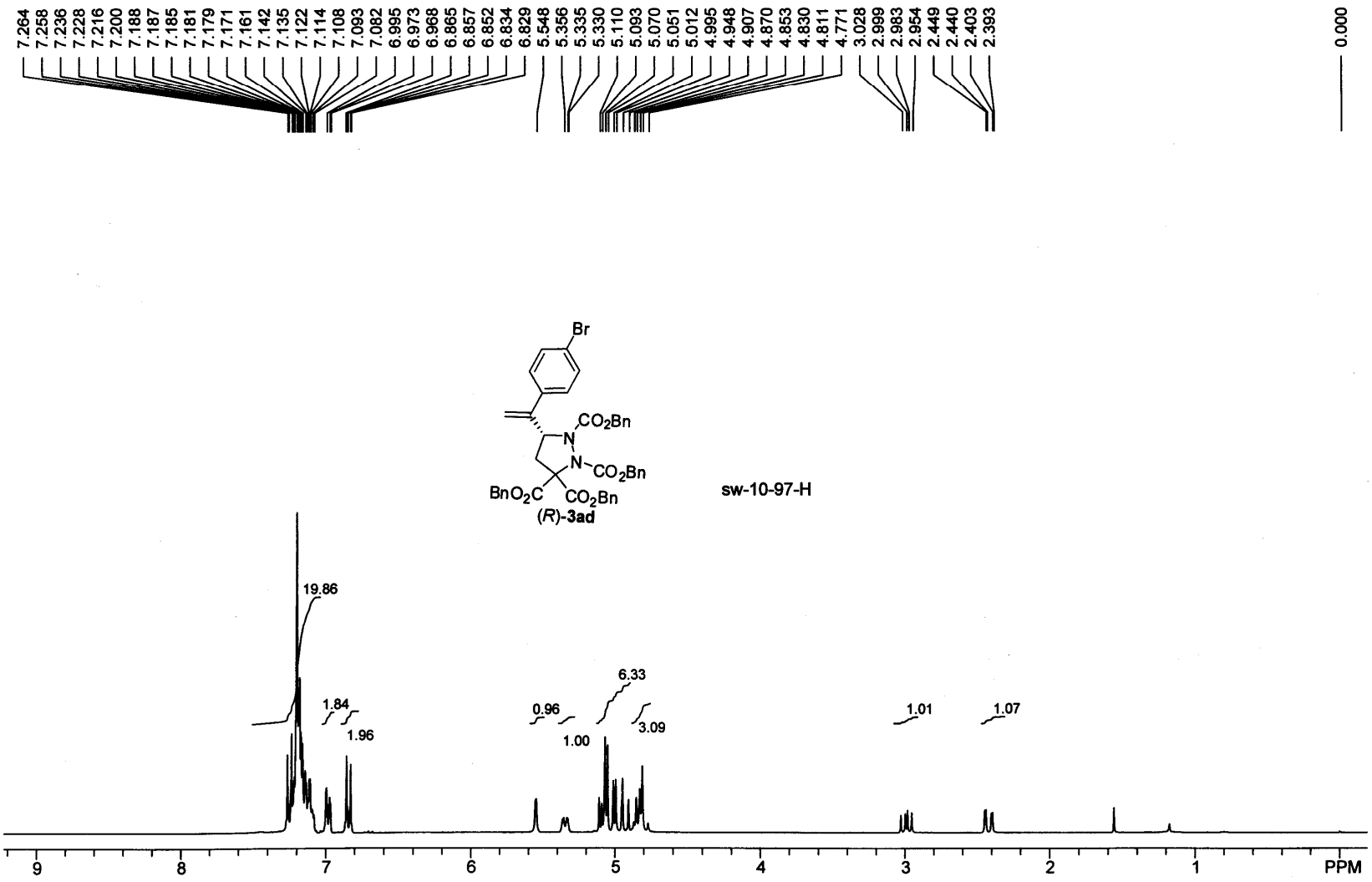
Sample Name:sw-10-88 od 80.che
Time:15:11
column:
Velocity:

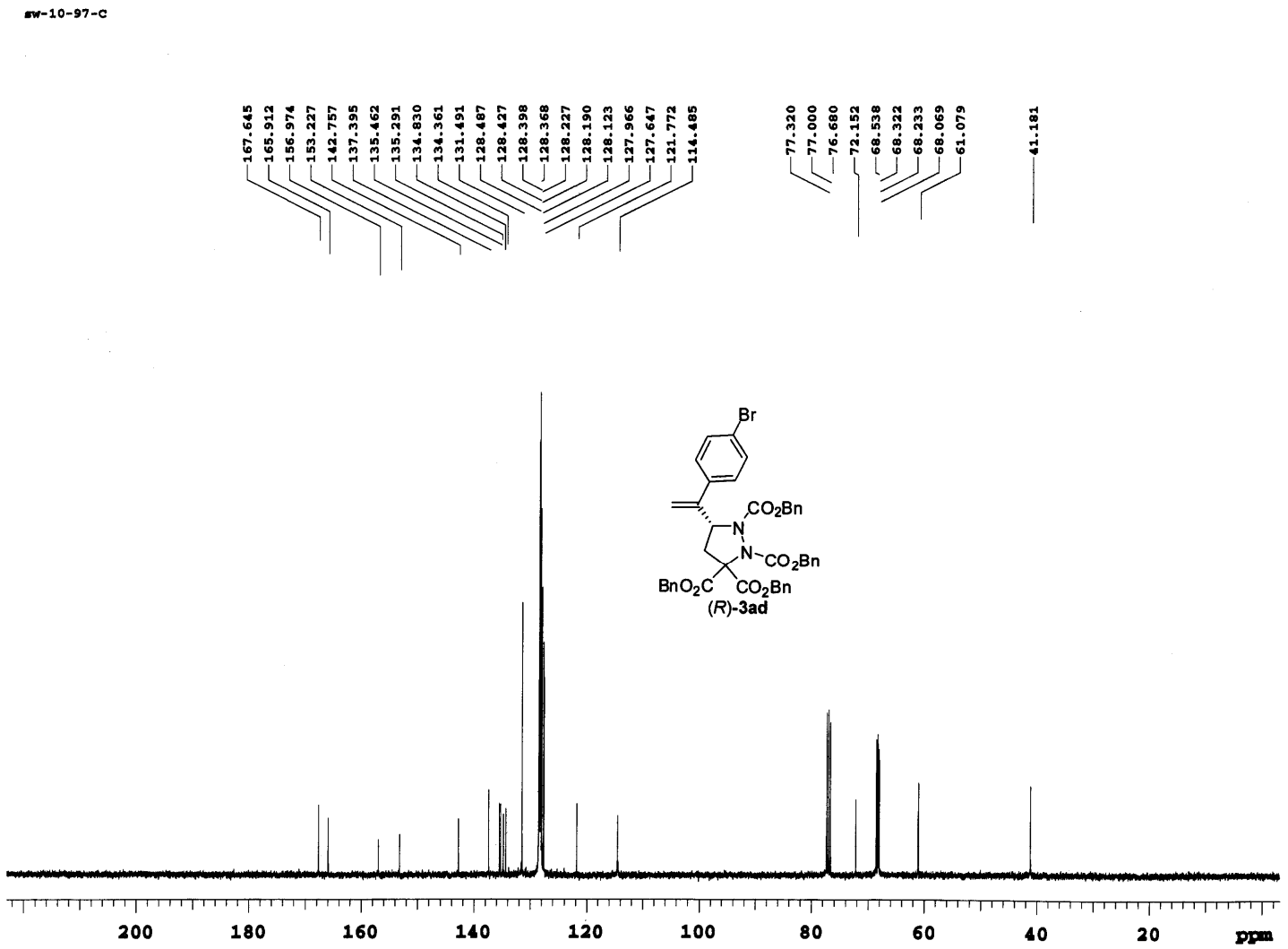
Date:2009-04-15
Method:
the mobile phase:
the detection wavelength:

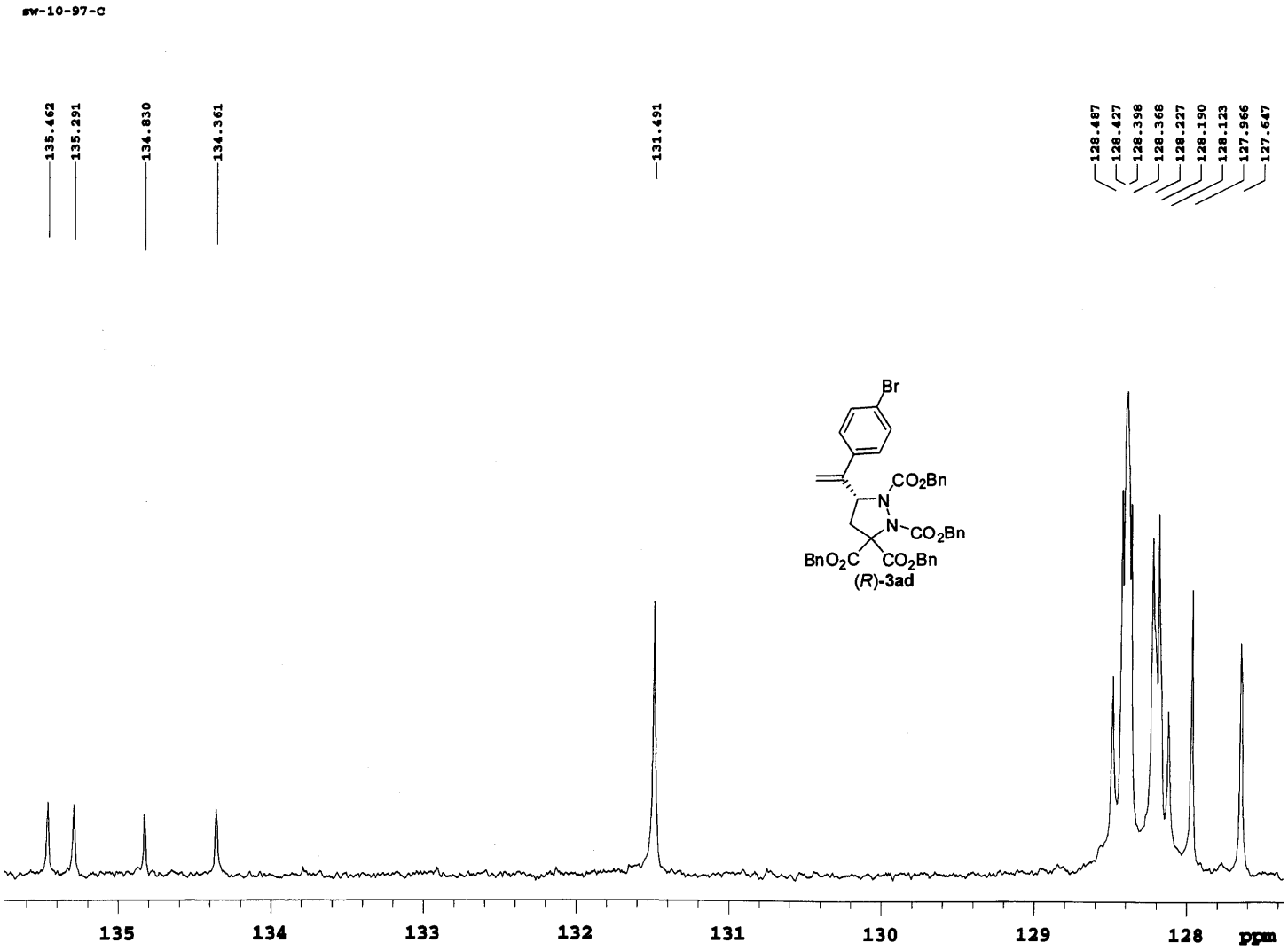


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	7.977	1265615.6	29961833.1	95.8093
2	2	10.227	35528.1	1310537.9	4.1907
Total			1301143.7	31272371.0	100.0000

ee = 9 2 %


7.264
7.258
7.236
7.228
7.216
7.200
7.188
7.187
7.185
7.181
7.179
7.171
7.161
7.142
7.135
7.122
7.114
7.108
7.093
7.082
6.995
6.973
6.968
6.865
6.857
6.852
6.834
6.829
5.548
5.356
5.335
5.330
5.110
5.093
5.070
5.051
5.012
4.995
4.948
4.907
4.870
4.853
4.830
4.811
4.771
3.028
2.999
2.983
2.954
2.449
2.440
2.403
2.393
0.000
Br
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ad
sw-10-97-H
19.86
1.84
1.96
0.96
1.00
6.33
3.09
1.01
1.07
9
8
7
6
5
4
3
2
1
PPM

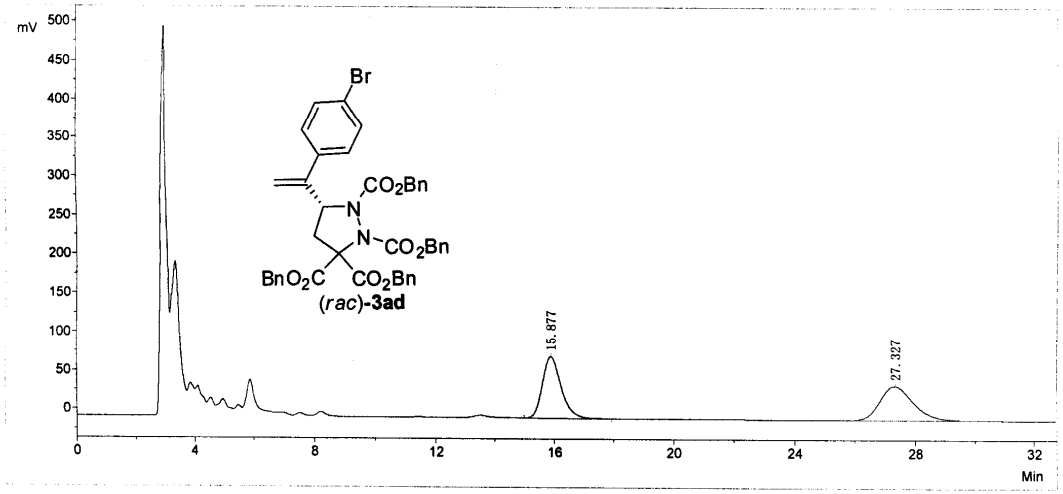

sw-10-97-c
167.645
165.912
156.974
153.227
142.757
137.395
135.462
135.291
134.830
134.361
131.491
128.487
128.427
128.398
128.368
128.227
128.190
128.123
127.966
127.647
121.772
114.485
77.320
77.000
76.680
72.152
68.538
68.322
68.233
68.069
61.079
41.181
Br
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ad
200
180
160
140
120
100
80
60
40
20
ppm


sw-10-97-c
135.462
135.291
134.830
134.361
131.491
128.487
128.427
128.398
128.368
128.227
128.190
128.123
127.966
127.647
Br
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ad
135
134
133
132
131
130
129
128
ppm

HPLC REPORT

Sample Name:sw-3-97rac ad 60 214.che
Time:09:19
column:
Velocity:

Date:2009-01-04
Method:
the mobile phase:
the detection wavelength:

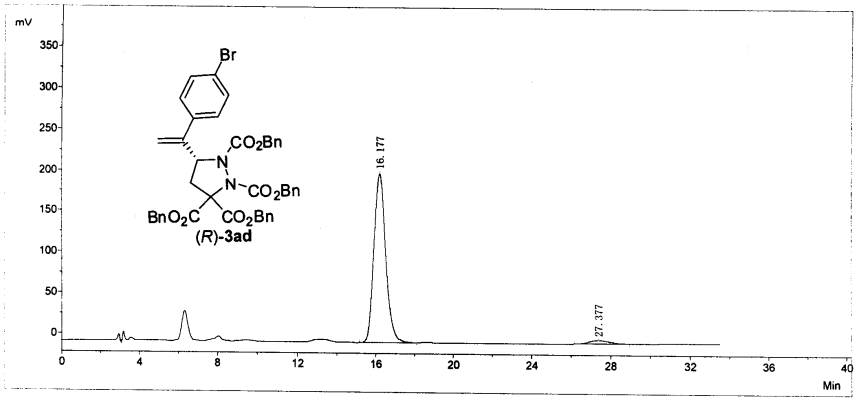


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	15.877	79190.7	3455157.9	50.3992
2	2	27.327	44054.1	3400423.4	49.6008
Total			123244.8	6855581.3	100.0000

HPLC REPORT

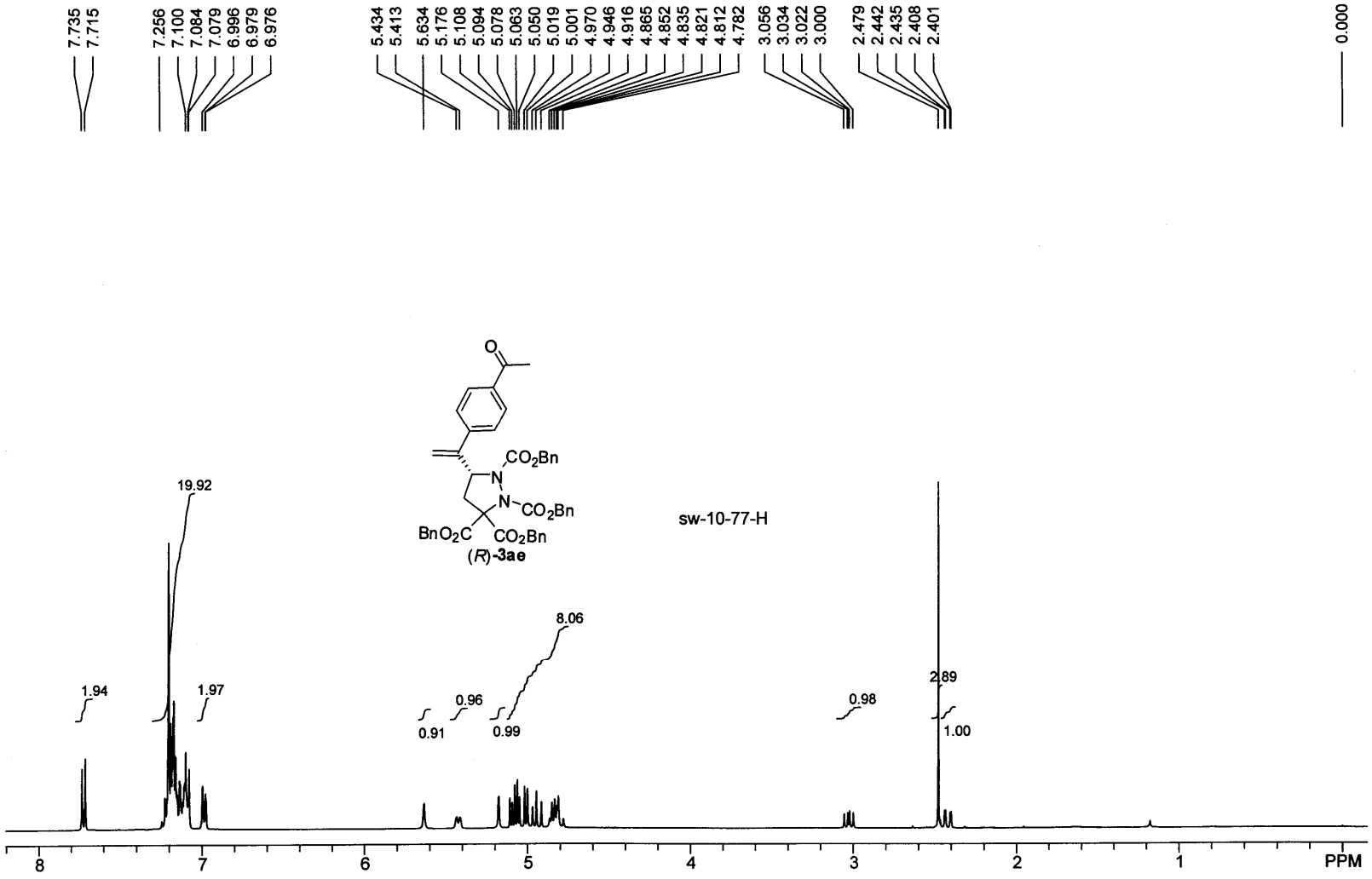
Sample Name:SW-10-97.che
Time:09:13
column:
Velocity:

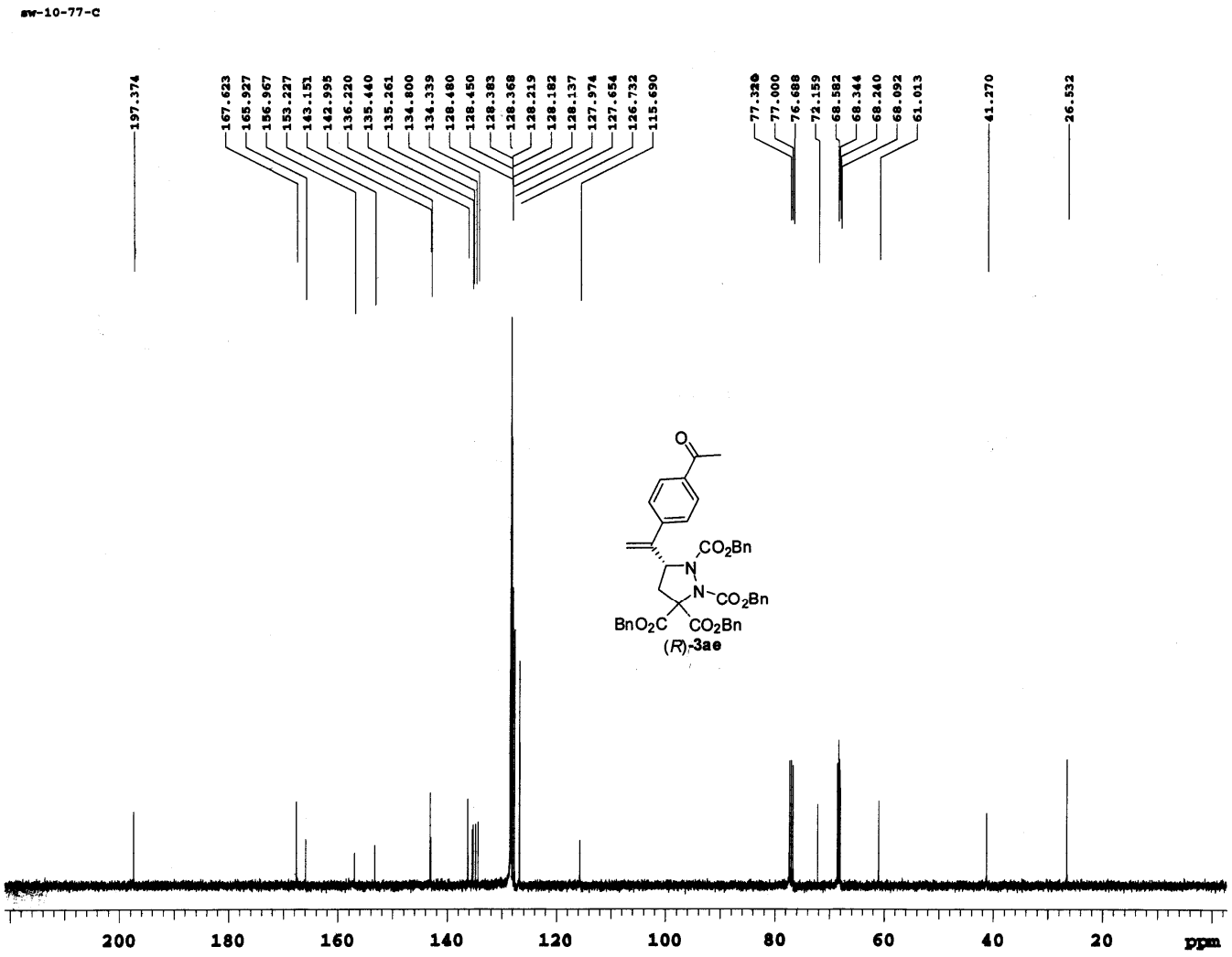
Date:2009-01-09
Method:
the mobile phase:
the detection wavelength:

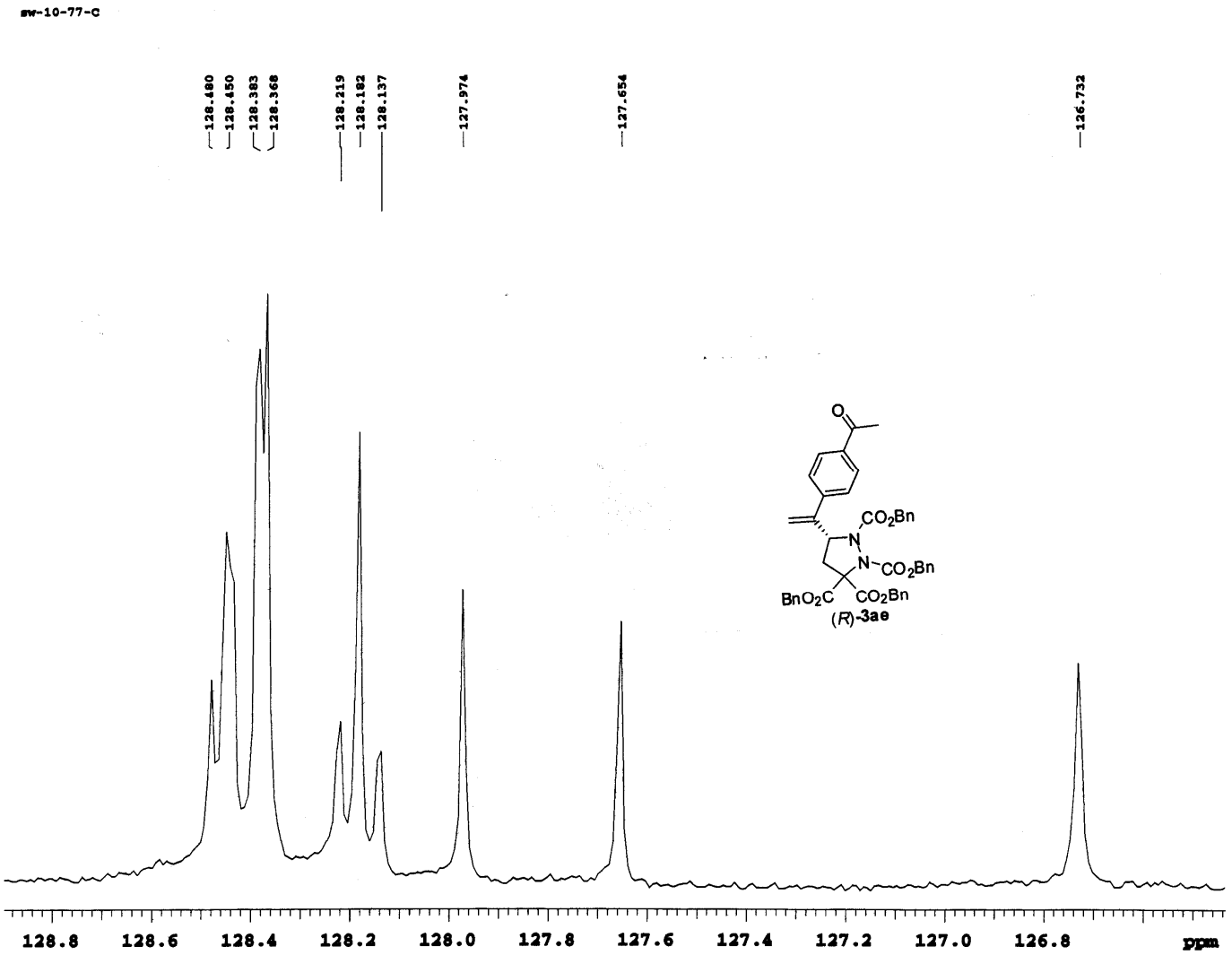


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	16.177	207681.3	8849893.7	96.6189
2	2	27.377	4398.0	309697.1	3.3811
Total			212079.3	9159590.8	100.0000

$ee = 96.6189 - 3.3811$
$= 93.2\%$


7.735
7.715
7.256
7.100
7.084
7.079
6.996
6.979
6.976
5.434
5.413
5.634
5.176
5.108
5.094
5.078
5.063
5.050
5.019
5.001
4.970
4.946
4.916
4.865
4.852
4.835
4.821
4.812
4.782
3.056
3.034
3.022
3.000
2.479
2.442
2.435
2.408
2.401
0.000
O
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ae
sw-10-77-H
19.92
1.94
1.97
0.91
0.96
0.99
8.06
0.98
2.89
1.00
8
7
6
5
4
3
2
1
PPM

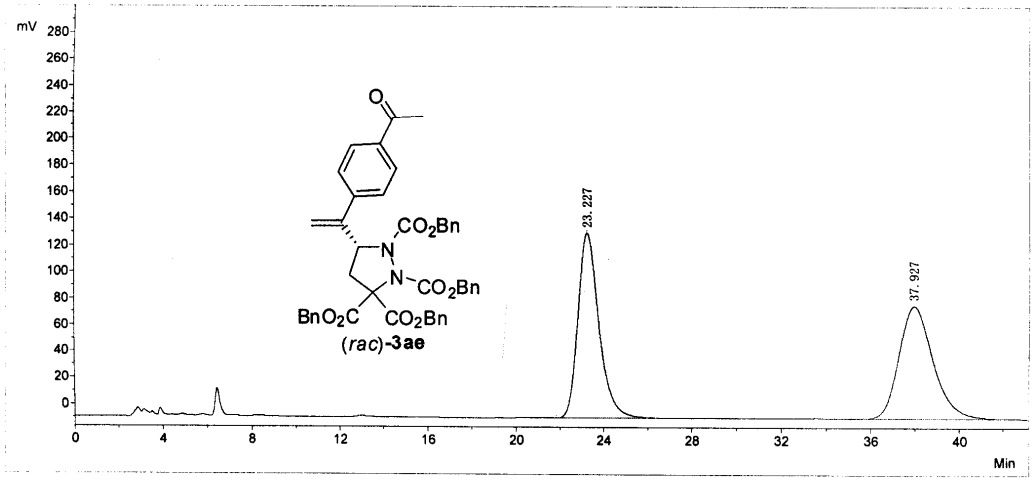

sw-10-77-c
197.374
167.623
165.927
156.967
153.227
143.151
142.995
136.220
135.440
135.261
134.800
134.339
128.480
128.450
128.383
128.368
128.219
128.182
128.137
127.974
127.654
126.732
115.690
77.328
77.000
76.688
72.159
68.582
68.344
68.240
68.092
61.013
41.270
26.532
O
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ae
200
180
160
140
120
100
80
60
40
20
ppm


sw-10-77-c
128.480
128.450
128.383
128.368
128.219
128.182
128.137
127.974
127.654
126.732
O
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ae
128.8
128.6
128.4
128.2
128.0
127.8
127.6
127.4
127.2
127.0
126.8
ppm

HPLC REPORT

Sample Name:sw-3-80rac ad 60 214.che
Time:14:47
column: AD-H
Velocity: 0.7

Date:2008-12-31
Method:
the mobile phase: 60/40
the detection wavelength: 214

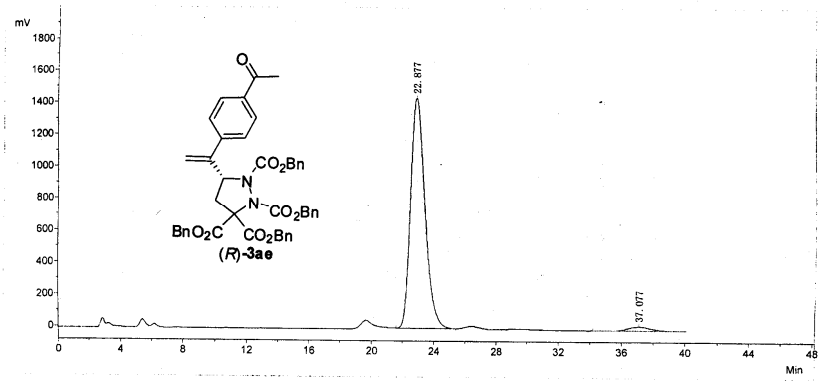


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	23.227	139146.8	9256496.2	50.4336
2	2	37.927	84904.2	9097341.1	49.5664
Total			224051.0	18353837.3	100.0000

HPLC REPORT

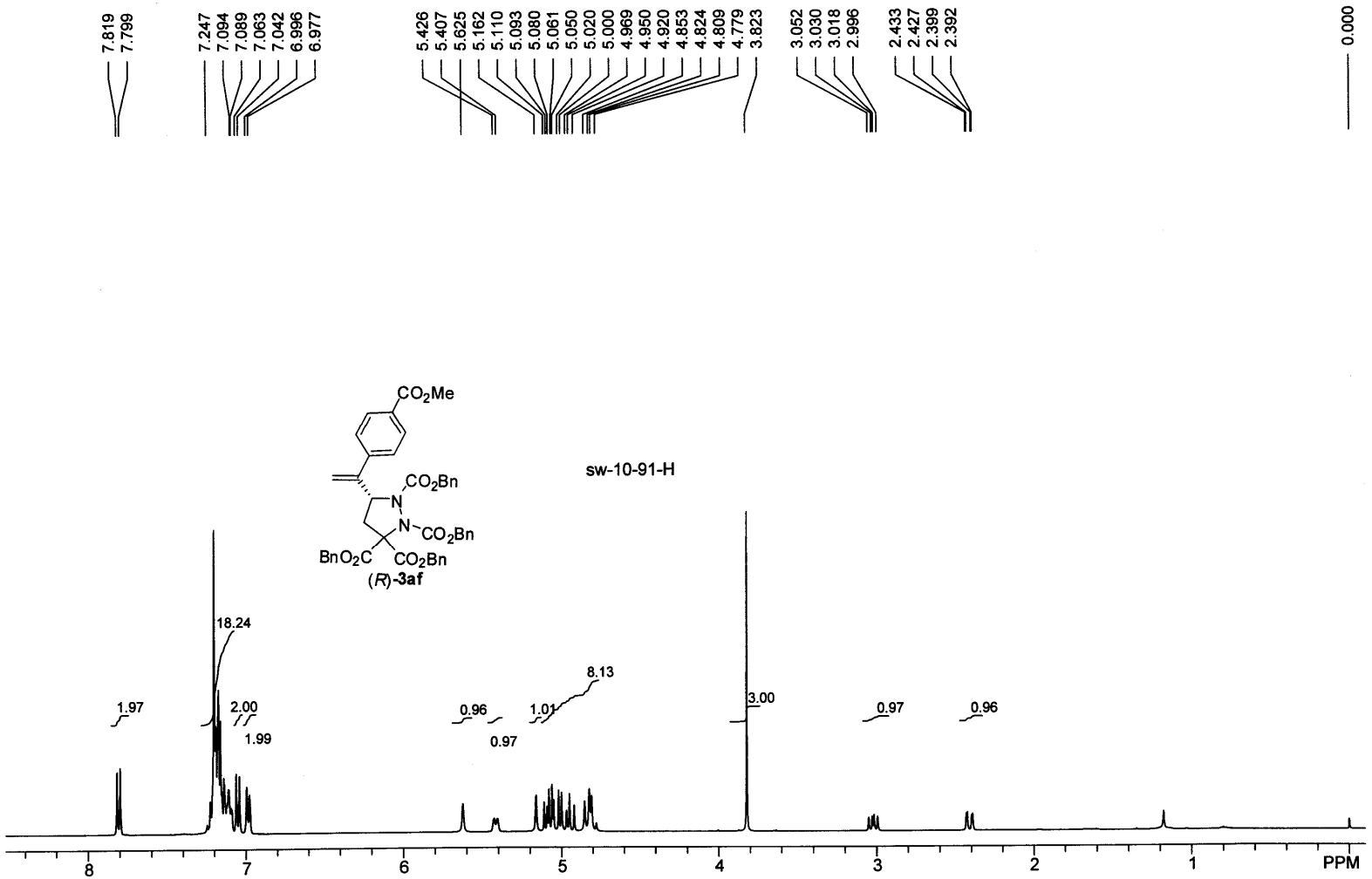
Sample Name:sw-10-77.che
Time:15:31
column:
Velocity:

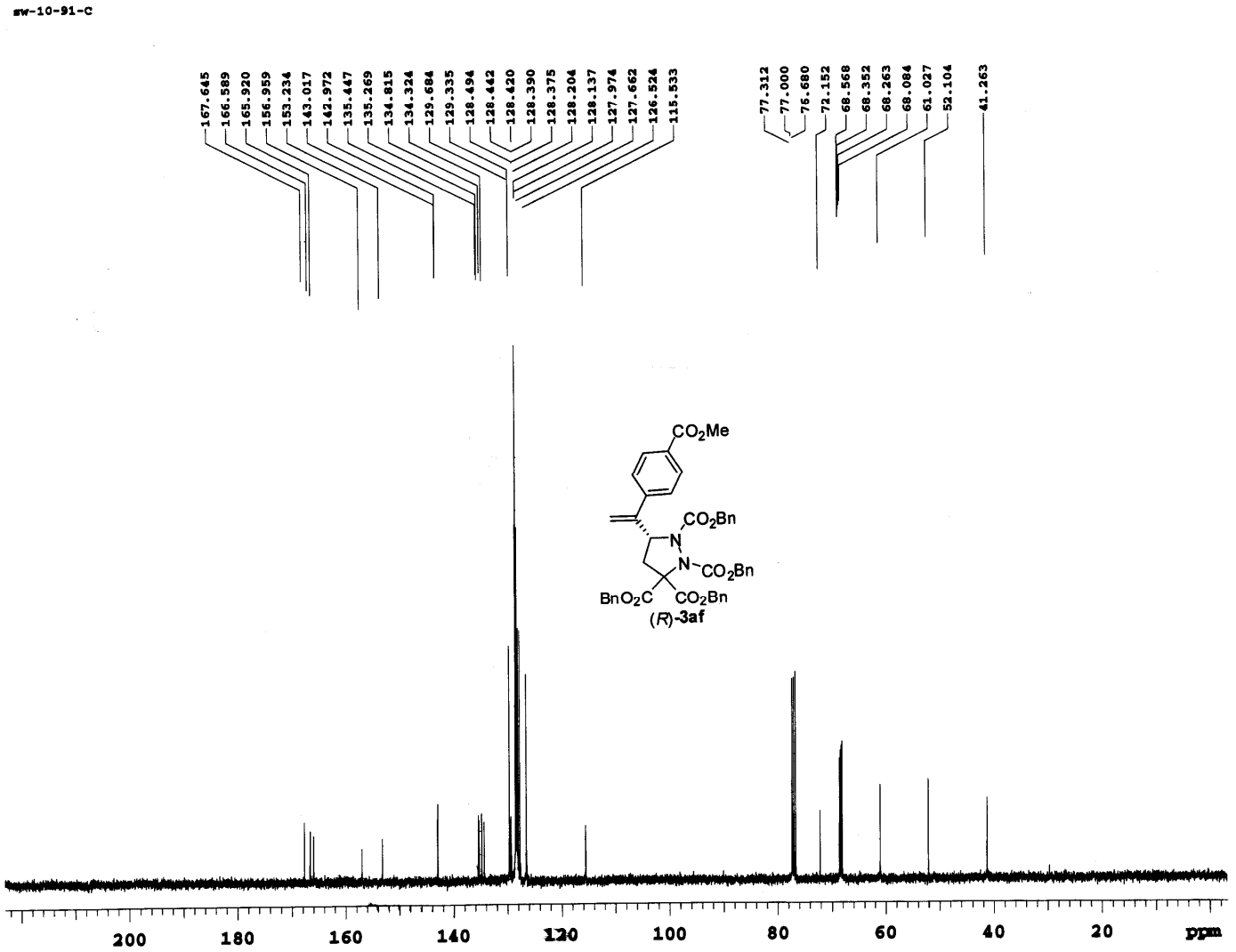
Date:2008-12-31
Method:
the mobile phase:
the detection wavelength:

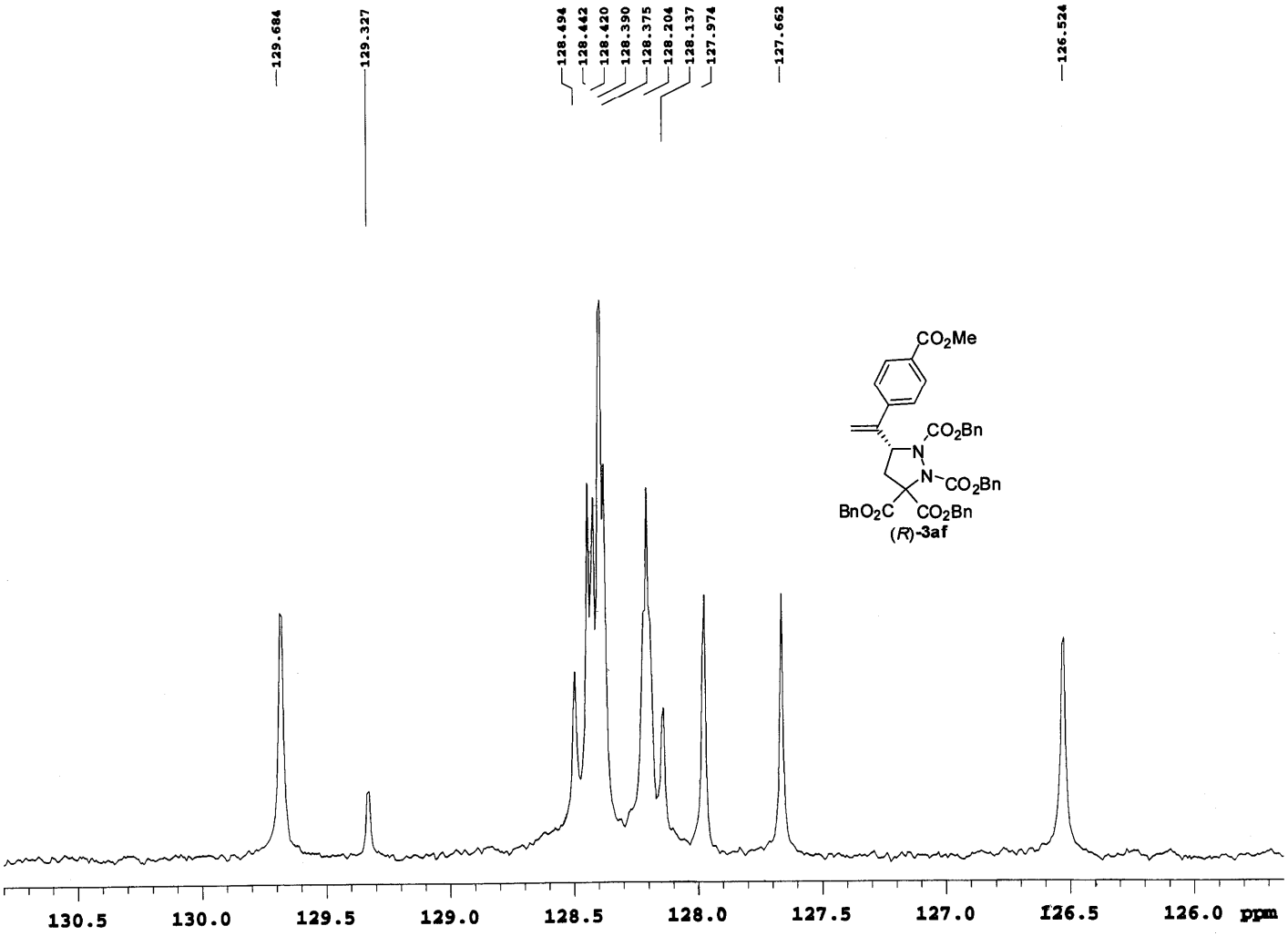


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	22.877	1437285.0	91897259.3	97.2311
2	2	37.077	25993.9	2617016.9	2.7689
Total			1463278.9	94514276.2	100.0000

ee = 97.2311 - 2.7689
= 94.5%


7.819
7.799
7.247
7.094
7.089
7.063
7.042
6.996
6.977
5.426
5.407
5.625
5.162
5.110
5.093
5.080
5.061
5.050
5.020
5.000
4.969
4.950
4.920
4.853
4.824
4.809
4.779
3.823
3.052
3.030
3.018
2.996
2.433
2.427
2.399
2.392
0.000
CO2Me
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3af
sw-10-91-H
18.24
1.97
2.00
1.99
0.96
0.97
1.01
8.13
3.00
0.97
0.96
8
7
6
5
4
3
2
1
PPM

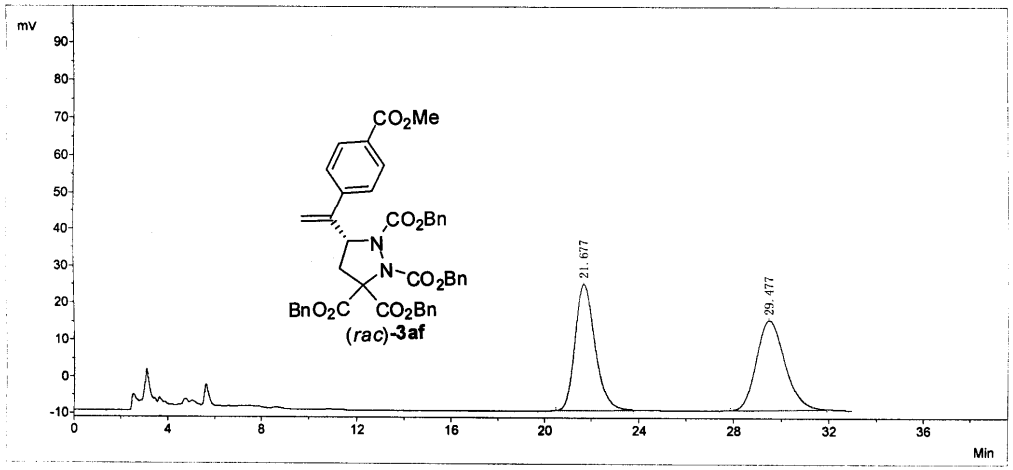

sw-10-91-c
167.645
166.589
165.920
156.959
153.234
143.017
142.972
135.447
135.269
134.815
134.324
129.684
129.335
128.494
128.442
128.420
128.390
128.375
128.204
128.137
127.974
127.662
126.524
115.533
77.312
77.000
76.680
72.152
68.568
68.352
68.263
68.084
61.027
52.104
41.263
CO2Me
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3af
200
180
160
140
120
100
80
60
40
20
ppm


129.684
129.327
128.494
128.442
128.420
128.390
128.375
128.204
128.137
127.974
127.662
126.524
CO2Me
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3af
130.5
130.0
129.5
129.0
128.5
128.0
127.5
127.0
126.5
126.0
ppm

HPLC REPORT

Sample Name:SW-3-75RAC AD 60.che
Time:10:01
column: AD-H
Velocity: 1

Date:2009-01-09
Method:
the mobile phase: 60/40
the detection wavelength: 220

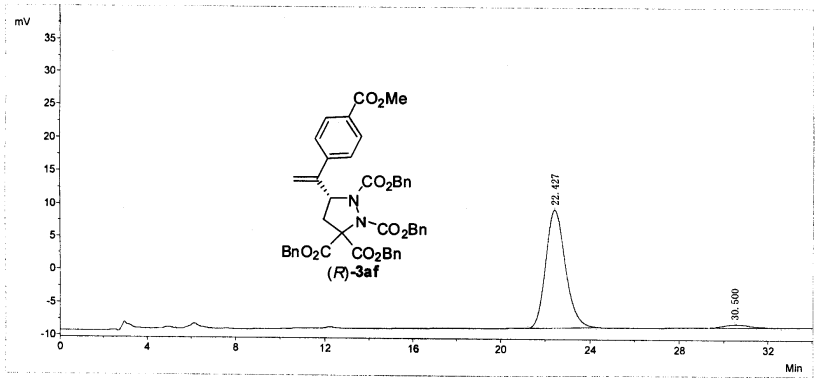


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	21.677	34113.7	2021188.7	50.0080
2	2	29.477	24296.2	2020542.8	49.9920
Total			58410.0	4041731.5	100.0000

HPLC REPORT

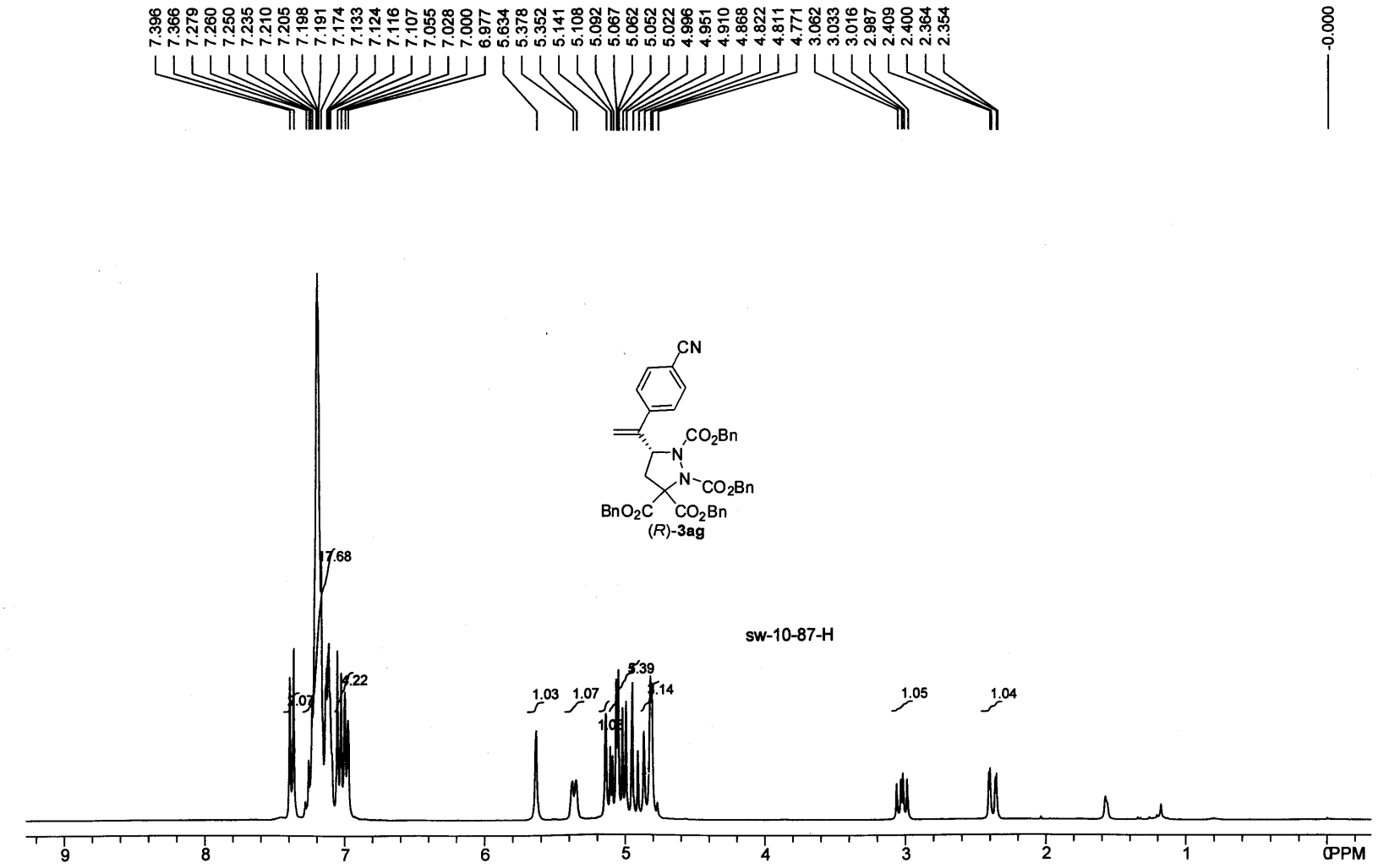
Sample Name:SW-10-91.che
Time:10:35
column:
Velocity:

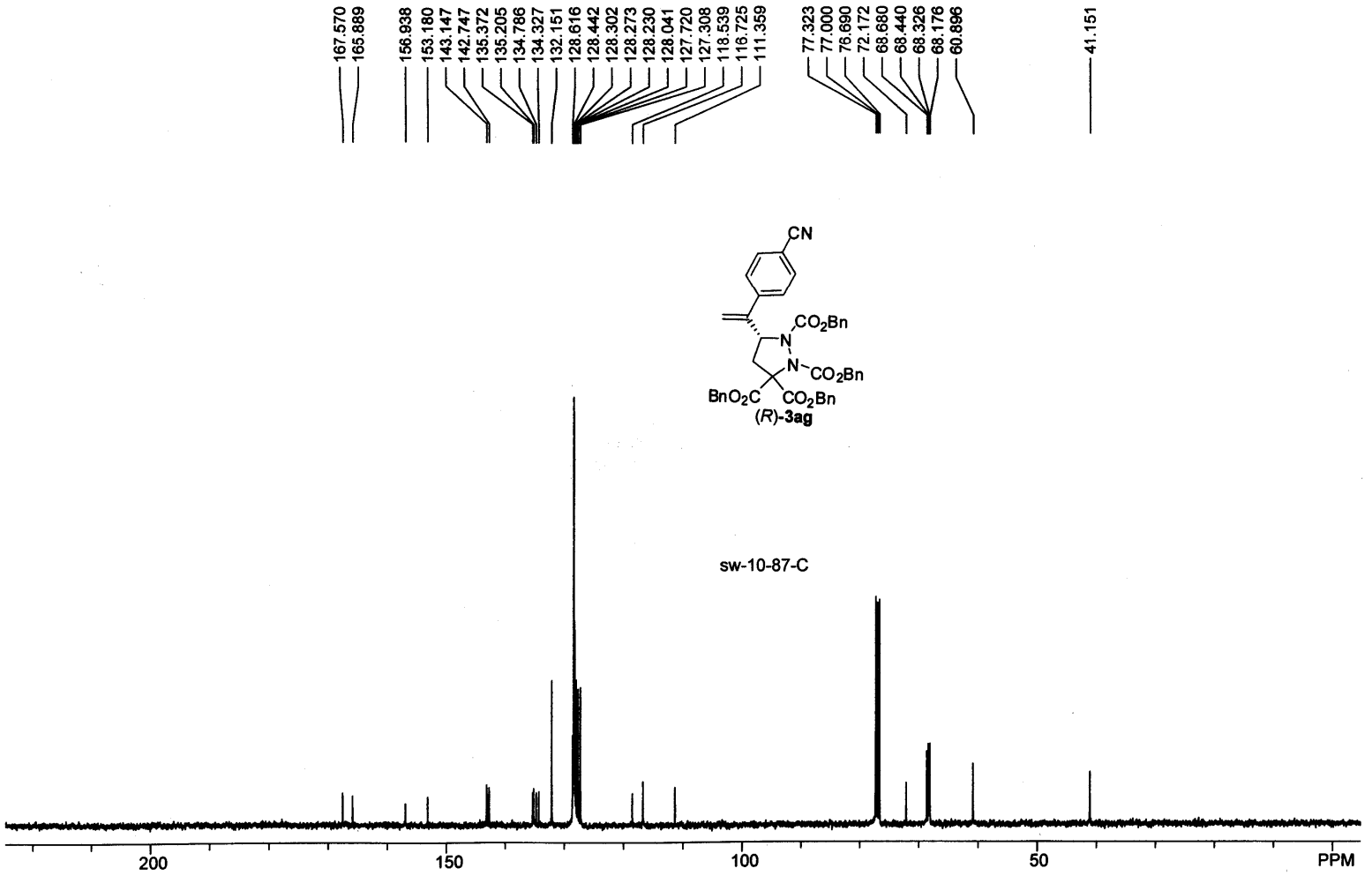
Date:2009-01-09
Method:
the mobile phase:
the detection wavelength:

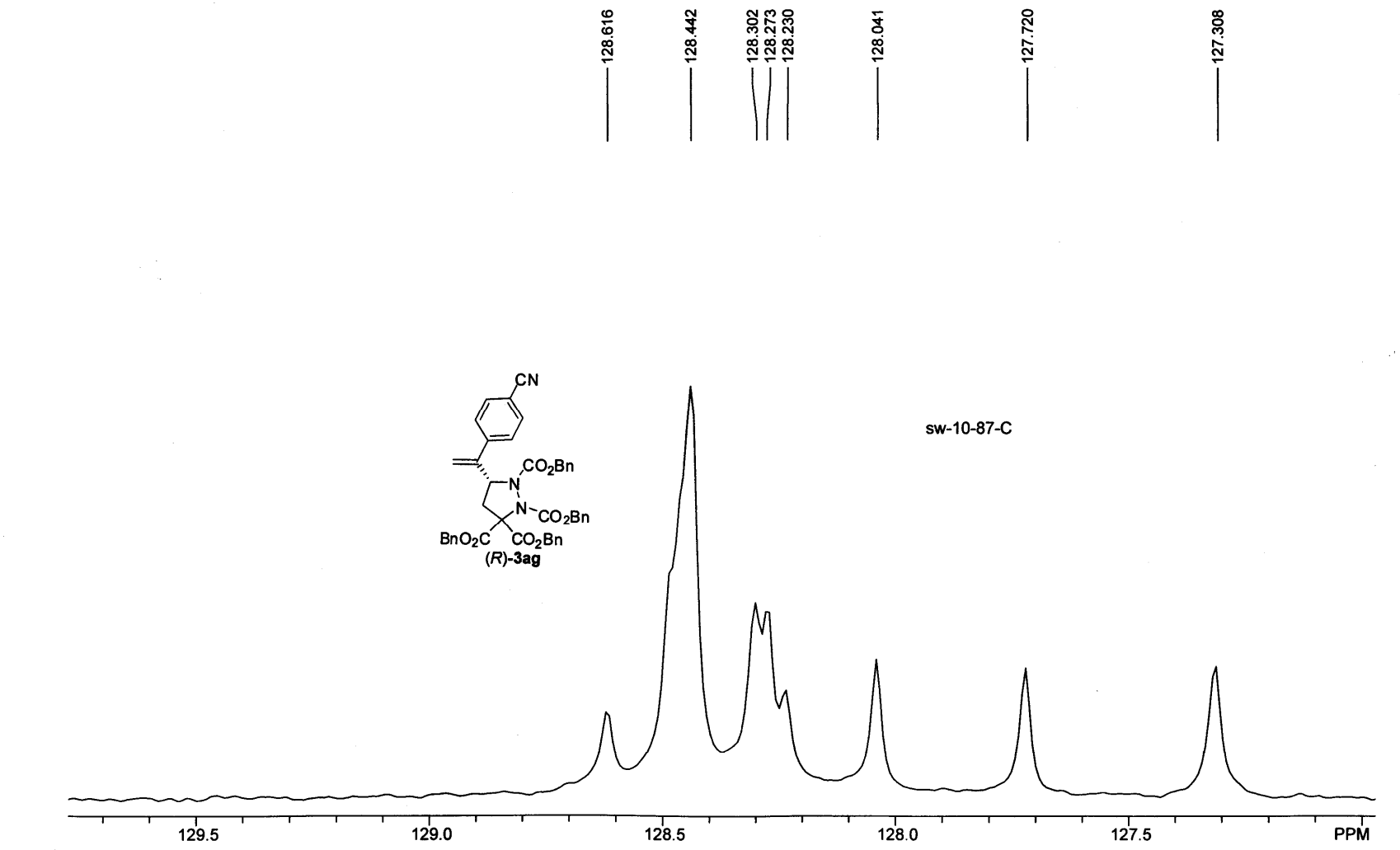


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	22.427	17884.0	1086237.6	96.4870
2	2	30.500	489.9	39549.4	3.5130
Total			18373.8	1125787.0	100.0000

ee = 96.4870 - 3.5130
= 93.0%


7.396
7.366
7.279
7.260
7.250
7.235
7.210
7.205
7.198
7.191
7.174
7.133
7.124
7.116
7.107
7.055
7.028
7.000
6.977
5.634
5.378
5.352
5.141
5.108
5.092
5.067
5.062
5.052
5.022
4.996
4.951
4.910
4.868
4.822
4.811
4.771
3.062
3.033
3.016
2.987
2.409
2.400
2.364
2.354
-0.000
CN
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ag
17.68
sw-10-87-H
1.03
1.07
5.39
5.14
1.05
1.04
9
8
7
6
5
4
3
2
1
0PPM

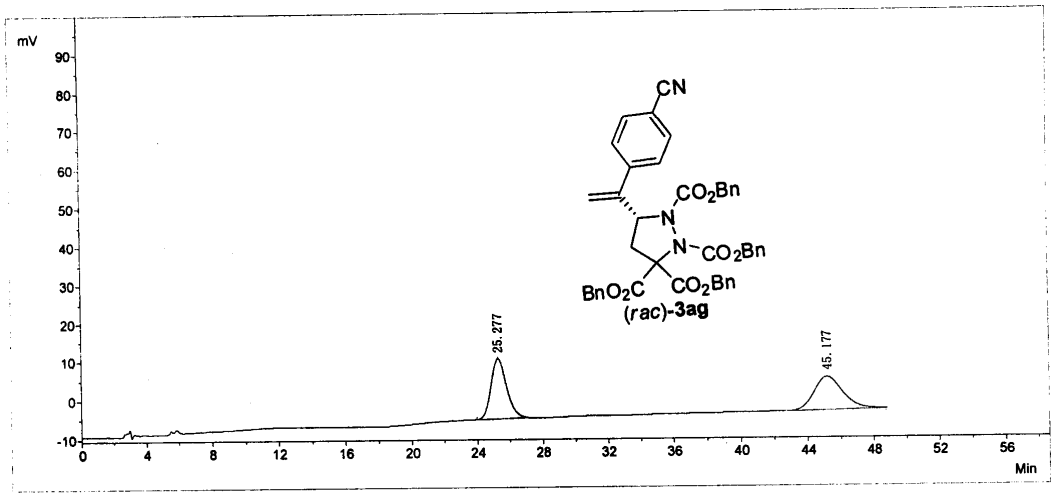

167.570
165.889
156.938
153.180
143.147
142.747
135.372
135.205
134.786
134.327
132.151
128.616
128.442
128.302
128.273
128.230
128.041
127.720
127.308
118.539
116.725
111.359
77.323
77.000
76.690
72.172
68.680
68.440
68.326
68.176
60.896
41.151
CN
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ag
sw-10-87-C
200
150
100
50
PPM


128.616
128.442
128.302
128.273
128.230
128.041
127.720
127.308
CN
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ag
sw-10-87-C
129.5
129.0
128.5
128.0
127.5
PPM

HPLC REPORT

Sample Name:SW-3-81RAC AD 60 214.che
Time:11:09
column: AD-H
Velocity: 0.7

Date:2009-01-09
Method:
the mobile phase: 5/95
the detection wavelength: 214

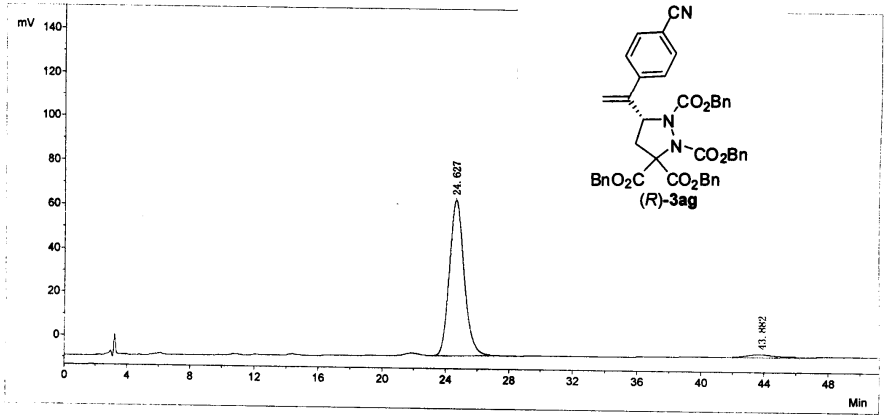


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	25.277	15450.9	1018191.1	50.1491
2	2	45.177	8470.5	1012135.9	49.8509
Total			23921.4	2030327.0	100.0000

HPLC REPORT

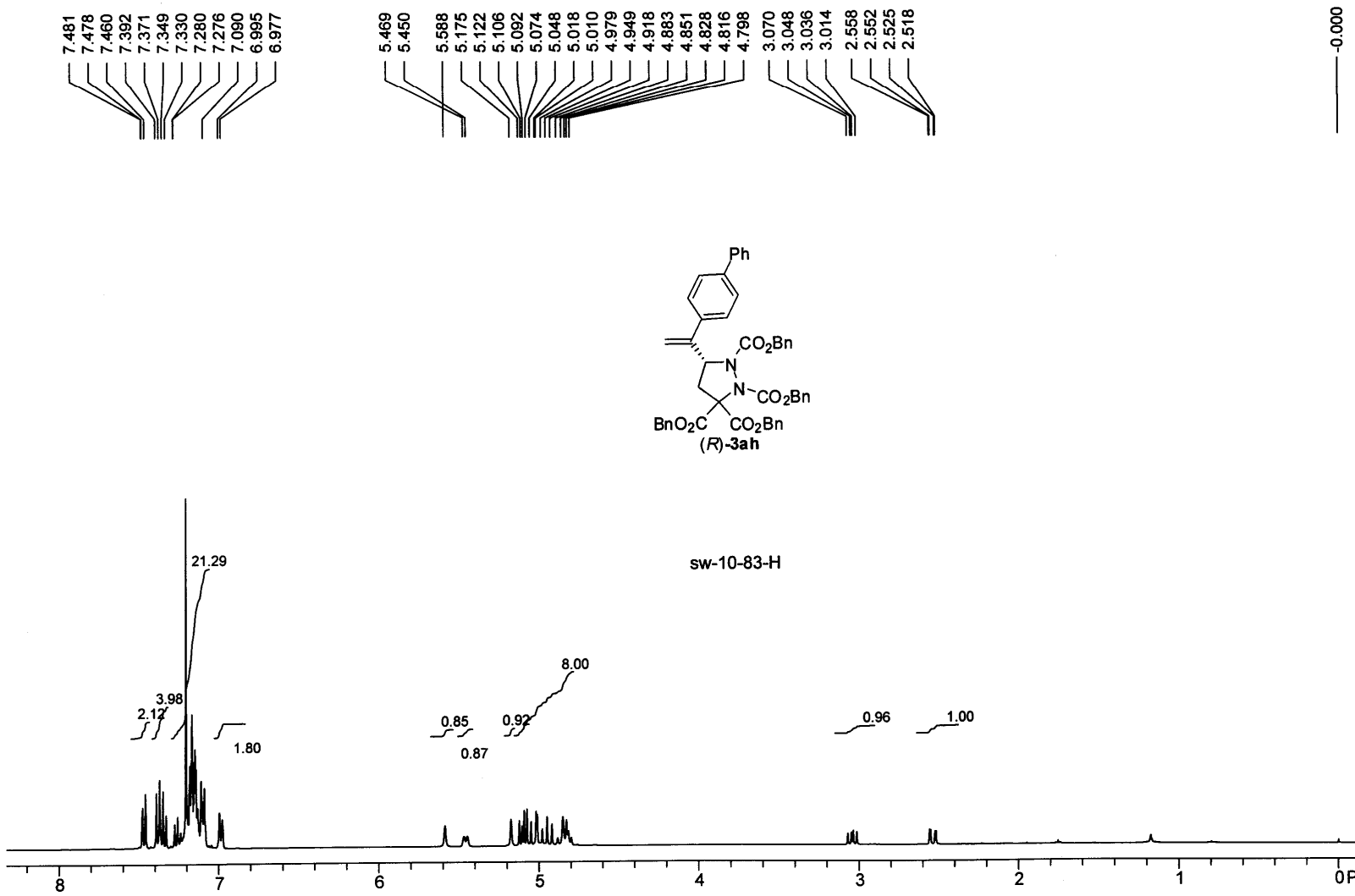
Sample Name:SW-10-87.che
Time:11:59
column:
Velocity:

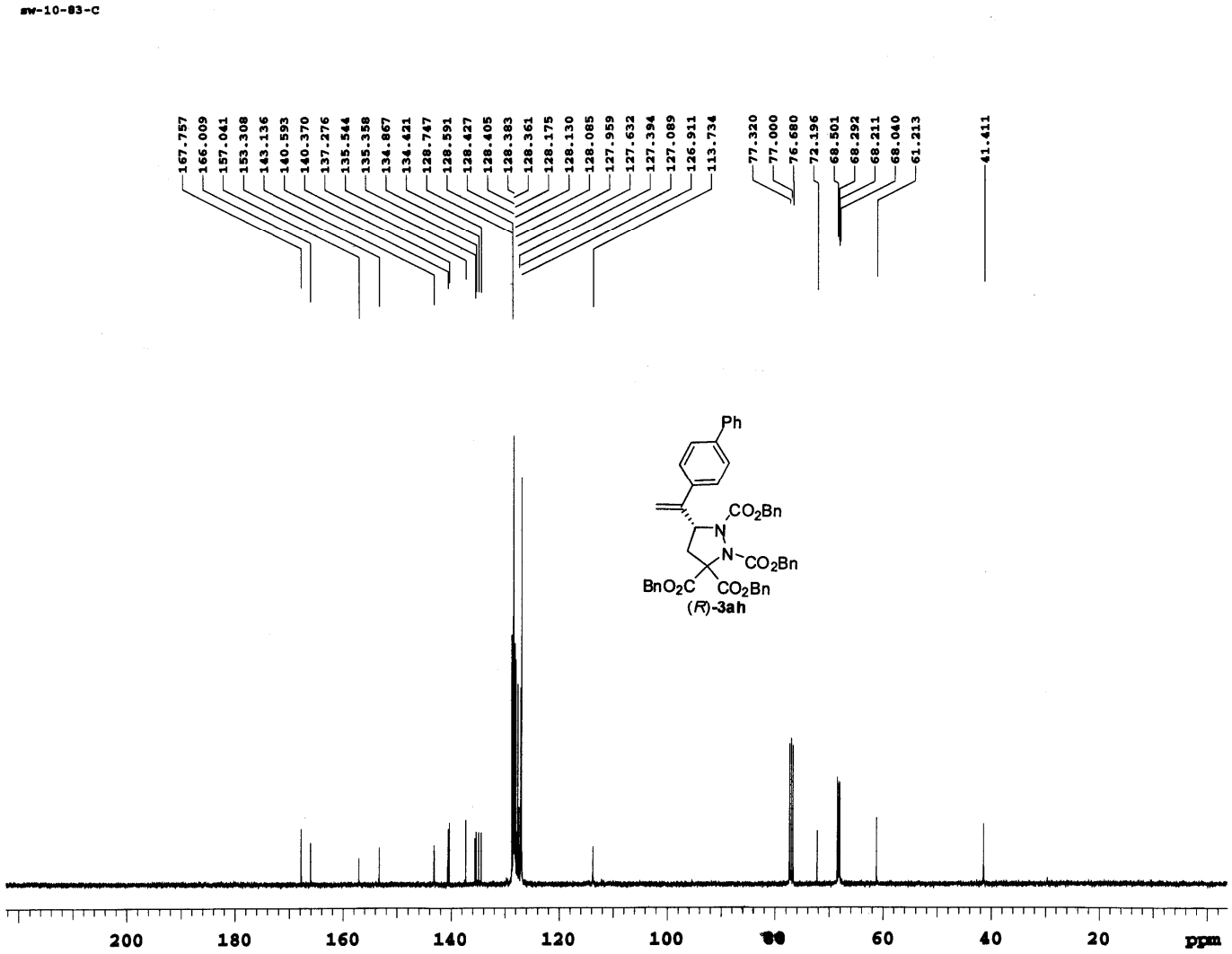
Date:2009-01-09
Method:
the mobile phase:
the detection wavelength:

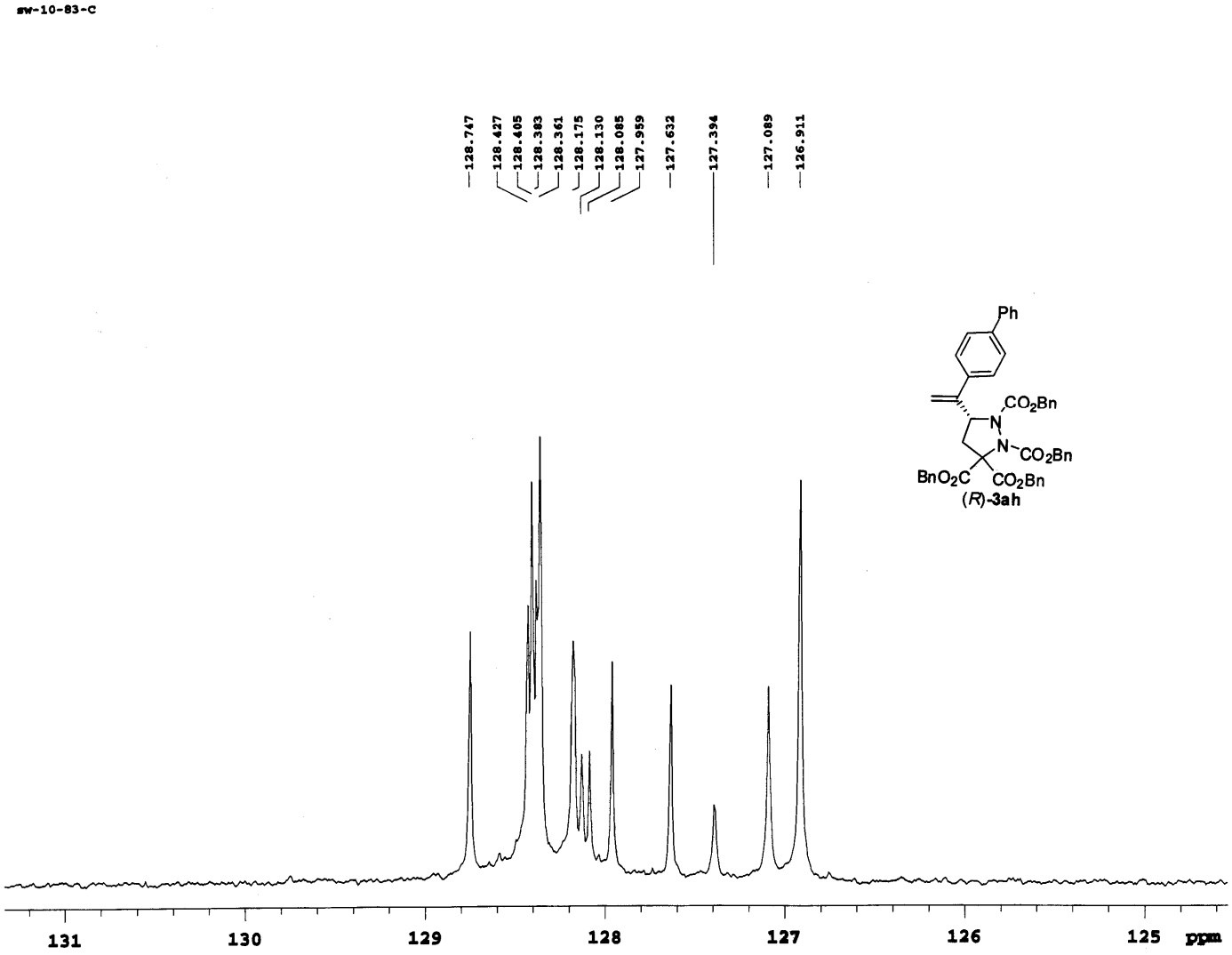


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	24.627	70809.3	4611251.7	97.0670
2	2	43.882	1251.9	139336.3	2.9330
Total			72061.2	4750588.0	100.0000

ee = 97.0670 - 2.9330
= 94.1%


7.481
7.478
7.460
7.392
7.371
7.349
7.330
7.280
7.276
7.090
6.995
6.977
5.469
5.450
5.588
5.175
5.122
5.106
5.092
5.074
5.048
5.018
5.010
4.979
4.949
4.918
4.883
4.851
4.828
4.816
4.798
3.070
3.048
3.036
3.014
2.558
2.552
2.525
2.518
-0.000
Ph
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ah
sw-10-83-H
21.29
3.98
2.12
1.80
0.85
0.87
0.92
8.00
0.96
1.00
8
7
6
5
4
3
2
1
0PPM

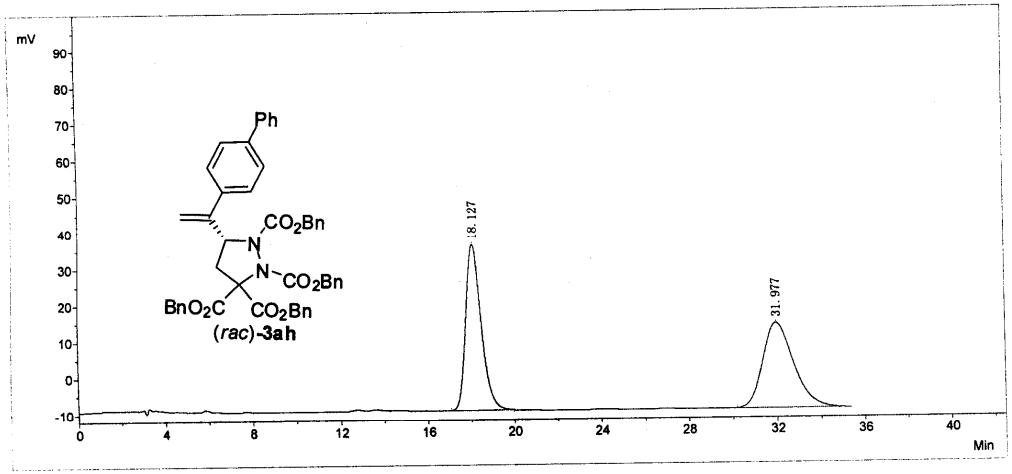

sw-10-83-C
167.757
166.009
157.041
153.308
143.136
140.593
140.370
137.276
135.544
135.358
134.867
134.421
128.747
128.591
128.427
128.405
128.383
128.361
128.175
128.130
128.085
127.959
127.632
127.394
127.089
126.911
113.734
77.320
77.000
76.680
72.196
68.501
68.292
68.211
68.040
61.213
41.411
Ph
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ah
200
180
160
140
120
100
80
60
40
20
ppm


sw-10-83-C
128.747
128.427
128.405
128.383
128.361
128.175
128.130
128.085
127.959
127.632
127.394
127.089
126.911
Ph
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ah
131
130
129
128
127
126
125
ppm

HPLC REPORT

Sample Name:SW-3-99RAC AD 60.che
Time:14:21
column: AD-H
Velocity: 0.7

Date:2009-01-09
Method:
the mobile phase: 6°/4°
the detection wavelength: 220

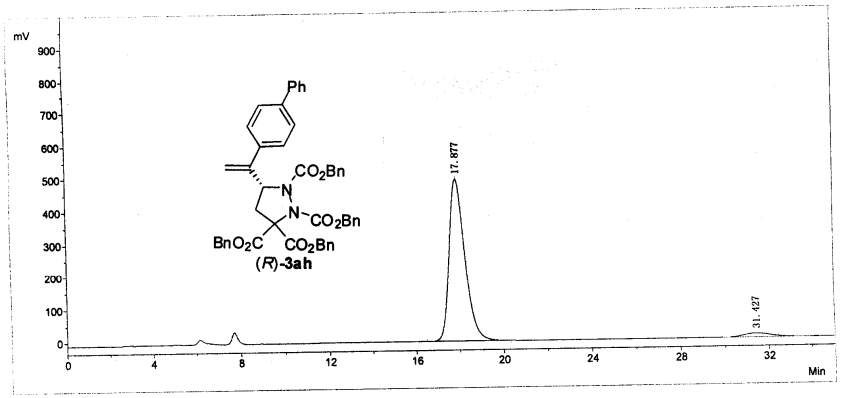


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	18.127	45498.4	2250618.2	49.9833
2	2	31.977	23266.0	2252126.5	50.0167
Total			68764.4	4502744.7	100.0000

HPLC REPORT

Sample Name:SW-10-83.che
Time:13:46
column:
Velocity:

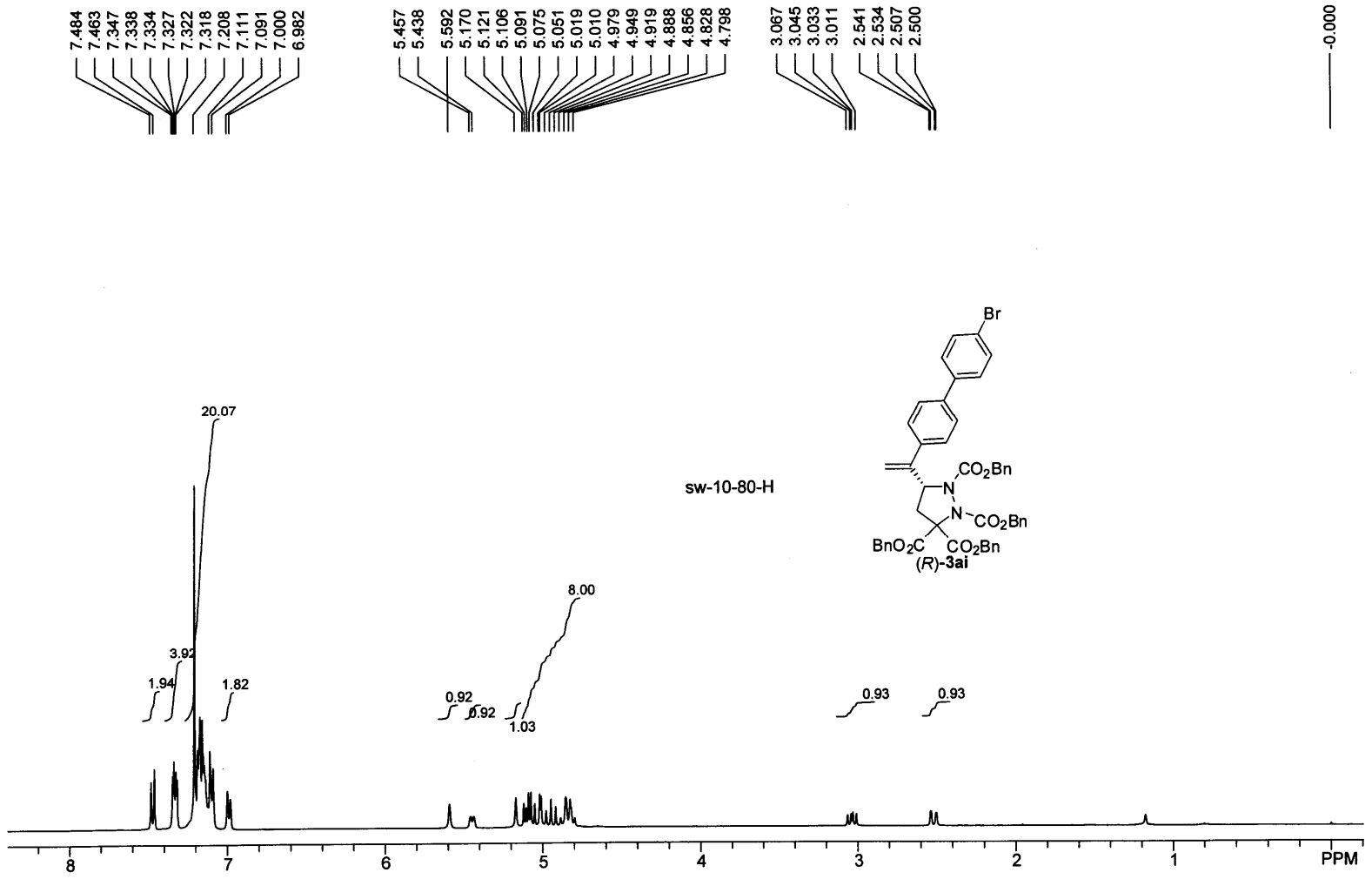
Date:2009-01-09
Method:
the mobile phase:
the detection wavelength:

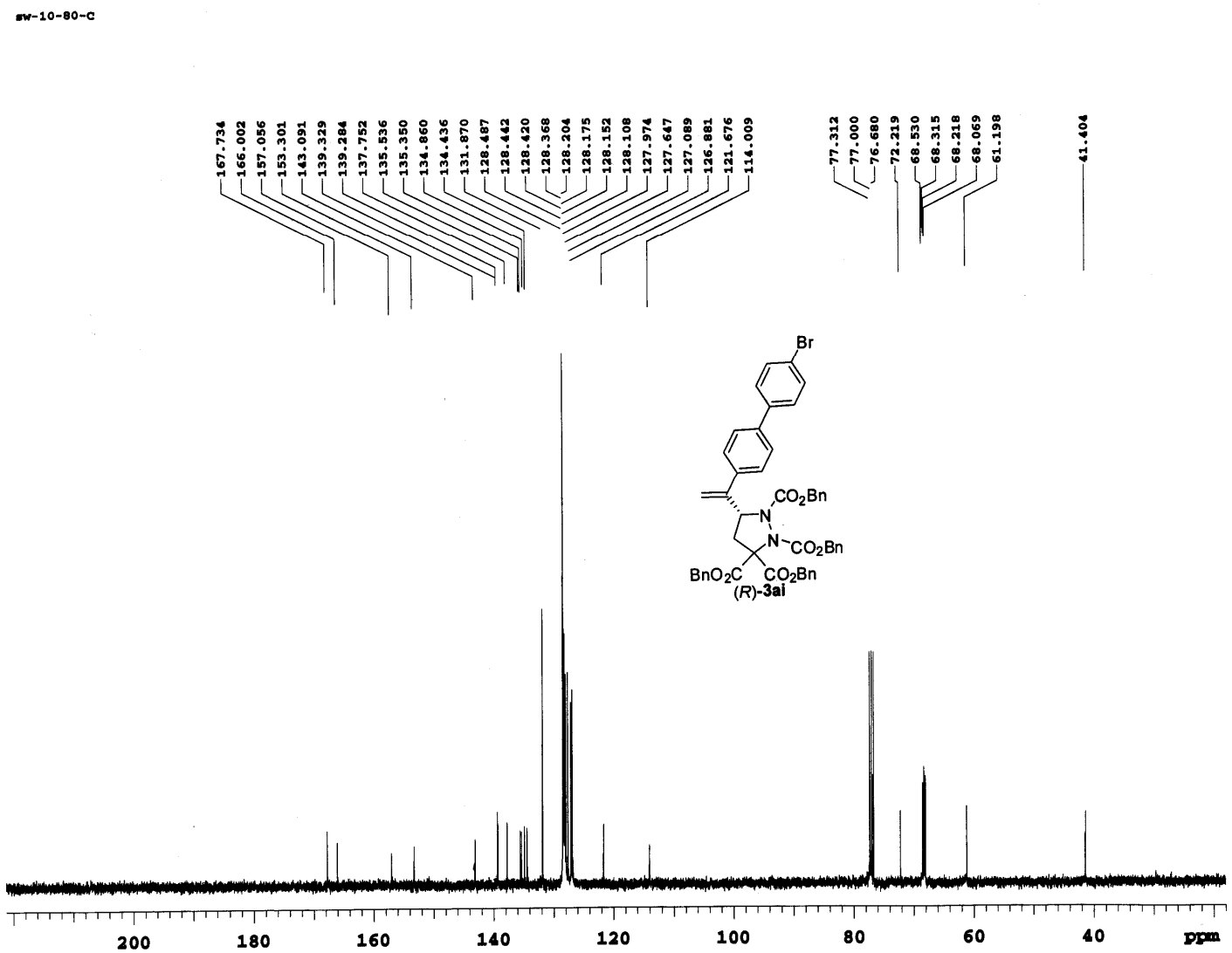


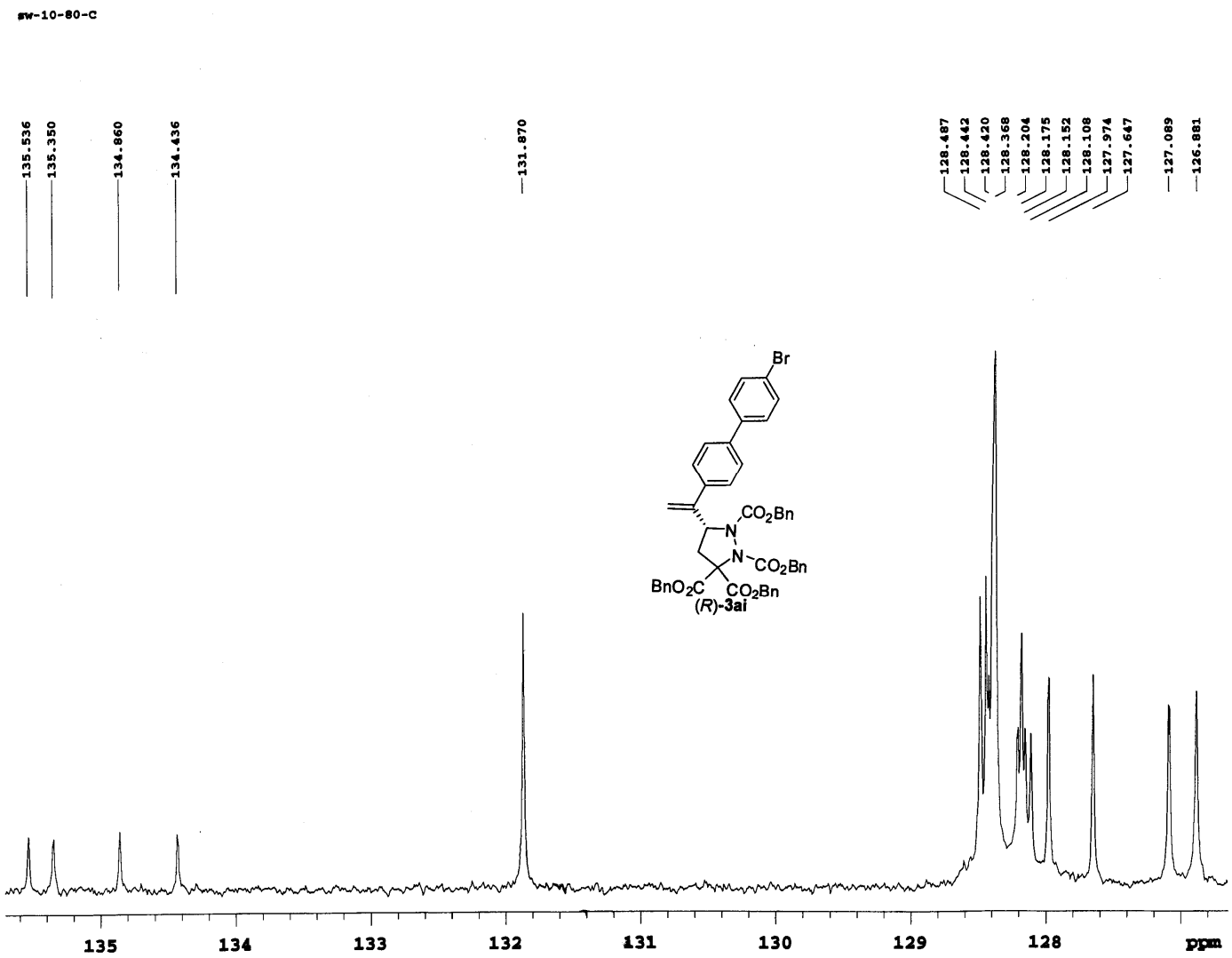
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	17.877	495674.5	24887511.8	95.7946
2	2	31.427	12010.2	1092562.9	4.2054
Total			507684.8	25980074.7	100.0000

$ee = 95.7946 - 4.2054$

$= 91.6\%$


7.484
7.463
7.347
7.338
7.334
7.327
7.322
7.318
7.208
7.111
7.091
7.000
6.982
5.457
5.438
5.592
5.170
5.121
5.106
5.091
5.075
5.051
5.019
5.010
4.979
4.949
4.919
4.888
4.856
4.828
4.798
3.067
3.045
3.033
3.011
2.541
2.534
2.507
2.500
-0.000
sw-10-80-H
Br
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ai
20.07
3.92
1.94
1.82
0.92
0.92
8.00
1.03
0.93
0.93
8
7
6
5
4
3
2
1
PPM

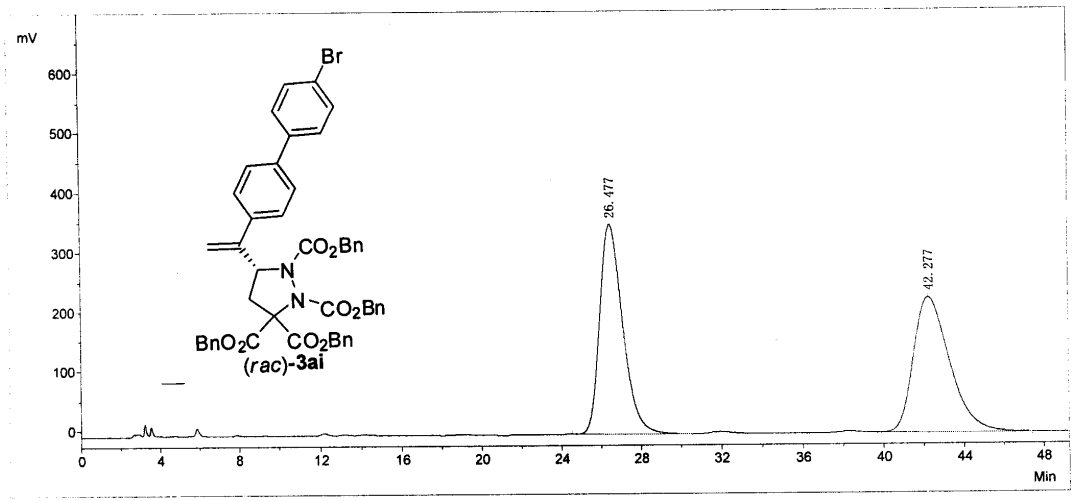

sw-10-80-C
167.734
166.002
157.056
153.301
143.091
139.329
139.284
137.752
135.536
135.350
134.860
134.436
131.870
128.487
128.442
128.420
128.368
128.204
128.175
128.152
128.108
127.974
127.647
127.089
126.881
121.676
114.009
77.312
77.000
76.680
72.219
68.530
68.315
68.218
68.069
61.198
41.404
Br
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ai
200
180
160
140
120
100
80
60
40
ppm


sw-10-80-c
135.536
135.350
134.860
134.436
131.870
128.487
128.442
128.420
128.368
128.204
128.175
128.152
128.108
127.974
127.647
127.089
126.881
Br
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ai
135
134
133
132
131
130
129
128
ppm

HPLC REPORT

Sample Name:SW-3-130RAC AD 60.che
Time:14:57
column: AD-H
Velocity: 0.7

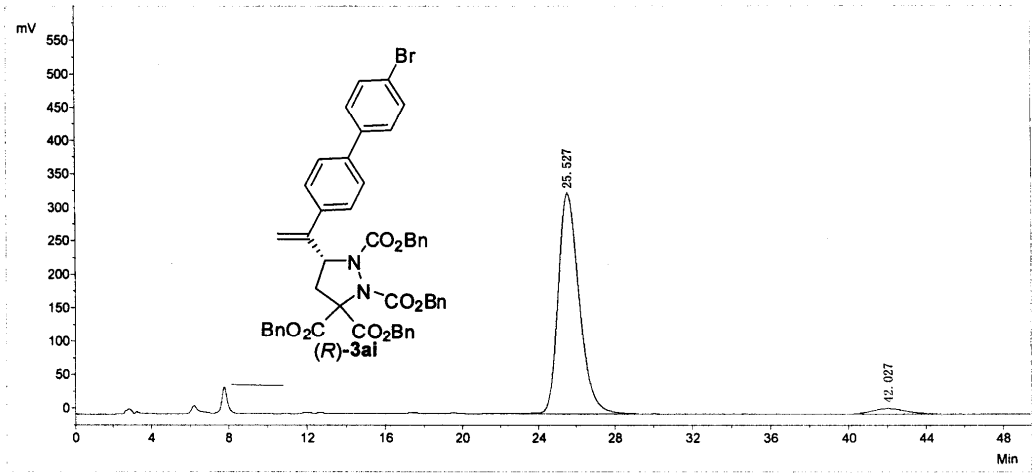
Date:2009-01-09
Method:
the mobile phase: 60/40
the detection wavelength: 230



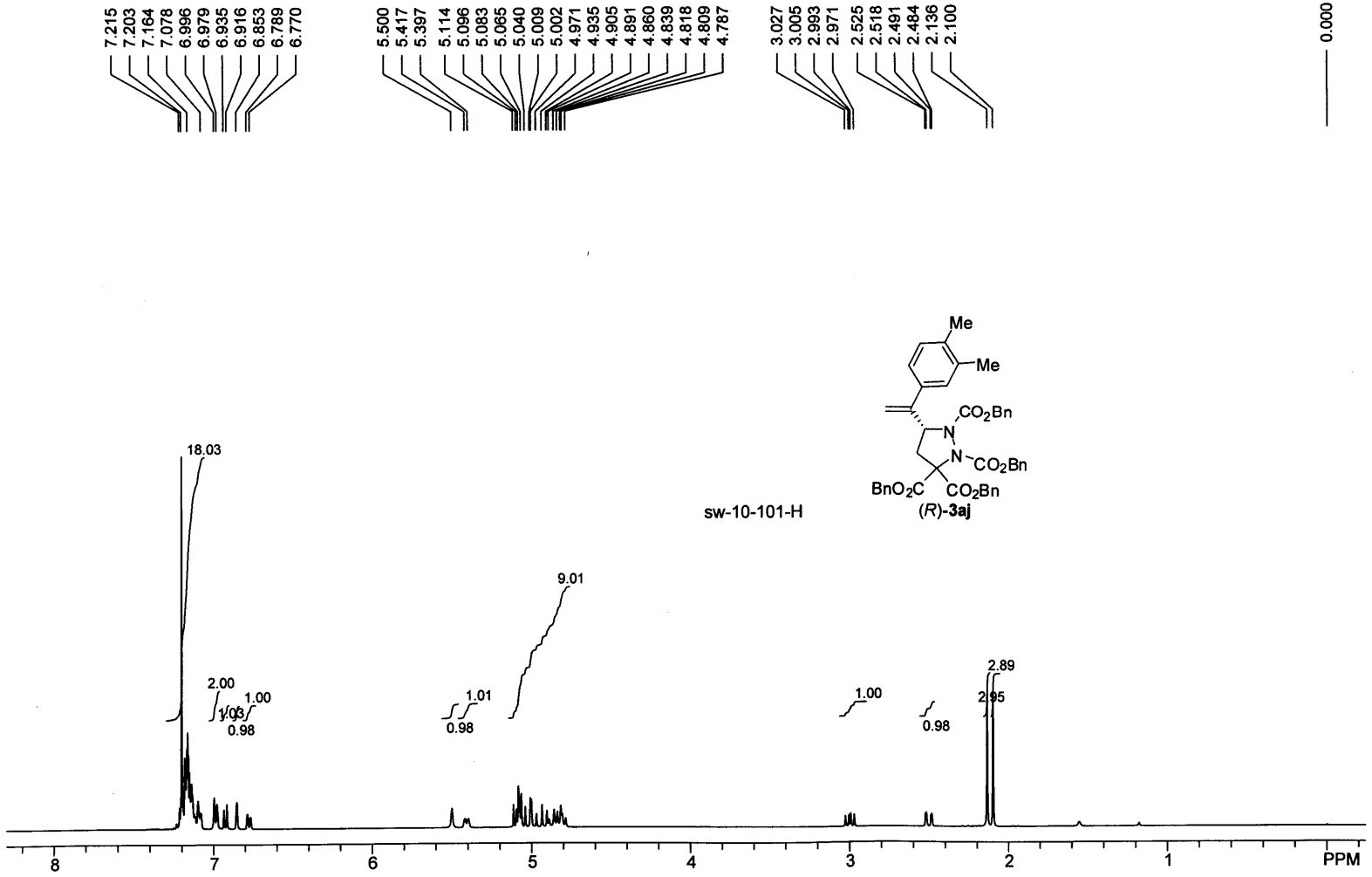
No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	26.477	351747.2	28106989.5	49.7823
2	2	42.277	227303.5	28352850.3	50.2177
Total			579050.7	56459839.8	100.0000

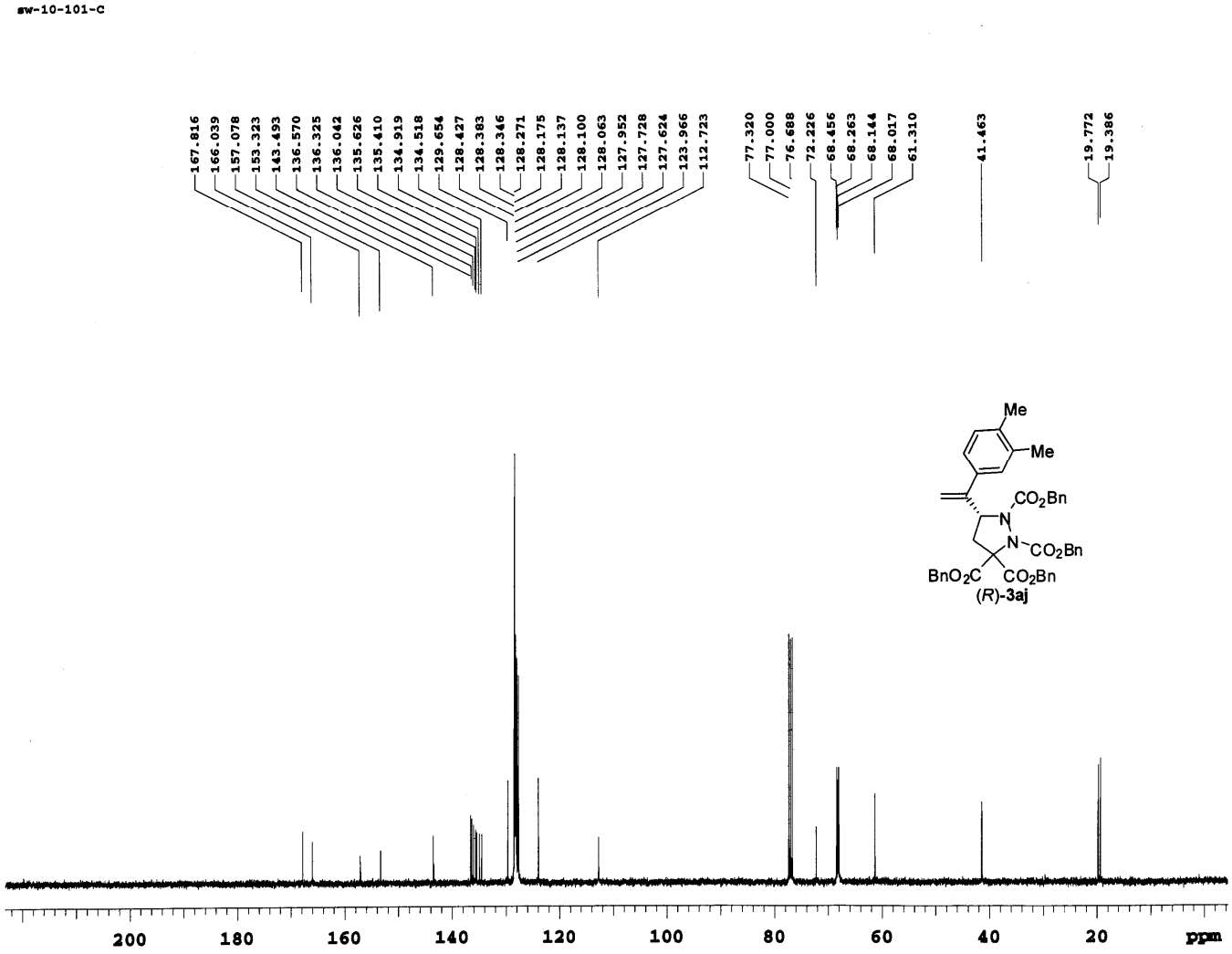
HPLC REPORT

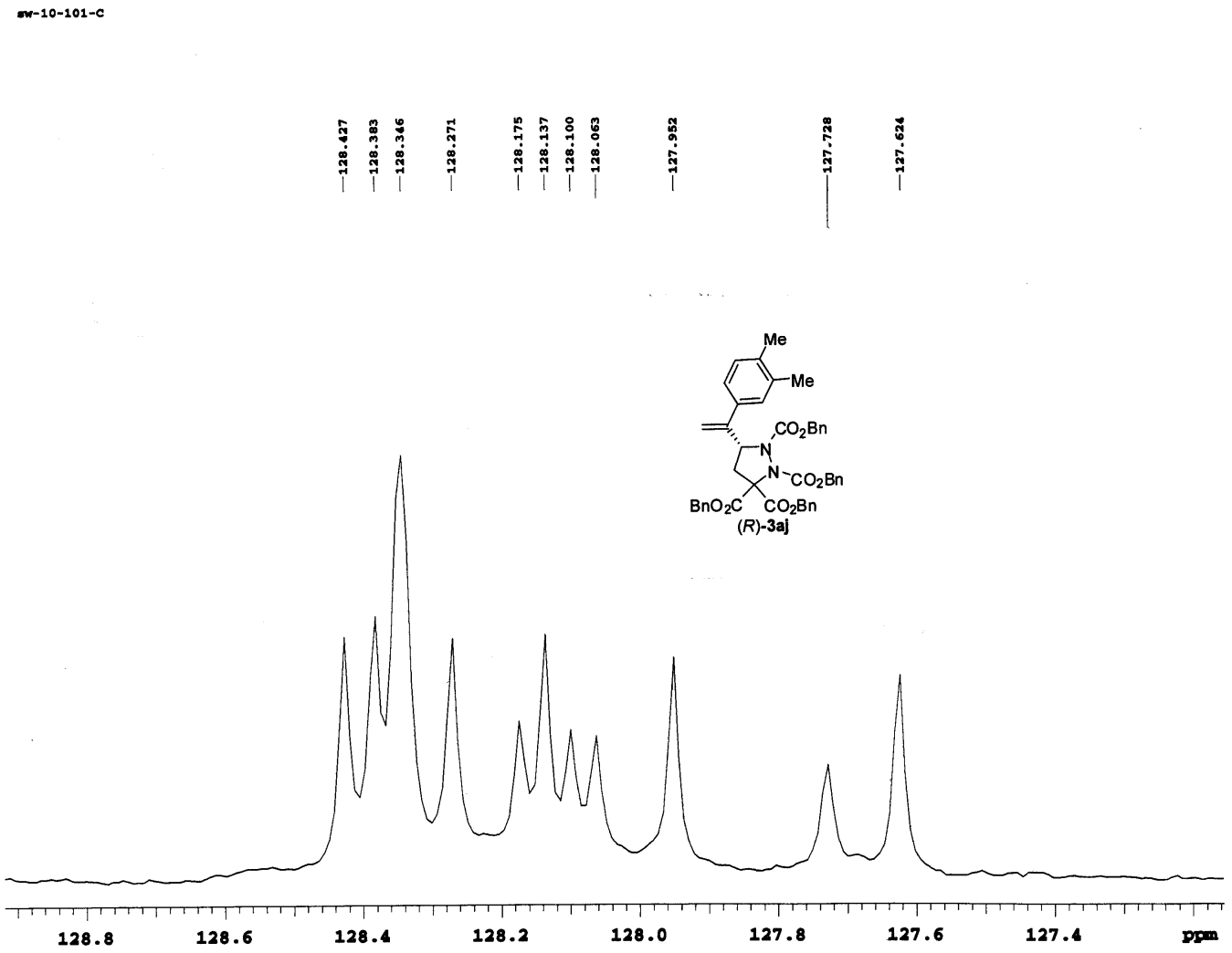
Sample Name:SW-10-80.che
Date:2009-01-09
Time:15:47
Method:
column:
the mobile phase:
Velocity:
the detection wavelength:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	25.527	328373.8	25087432.2	96.1737
2	2	42.027	8204.9	998102.3	3.8263
Total			336578.7	26085534.5	100.0000


7.215
7.203
7.164
7.078
6.996
6.979
6.935
6.916
6.853
6.789
6.770
5.500
5.417
5.397
5.114
5.096
5.083
5.065
5.040
5.009
5.002
4.971
4.935
4.905
4.891
4.860
4.839
4.818
4.809
4.787
3.027
3.005
2.993
2.971
2.525
2.518
2.491
2.484
2.136
2.100
0.000
Me
Me
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
sw-10-101-H
(R)-3aj
18.03
2.00
1.03
1.00
0.98
1.01
0.98
9.01
1.00
0.98
2.89
2.95
8
7
6
5
4
3
2
1
PPM

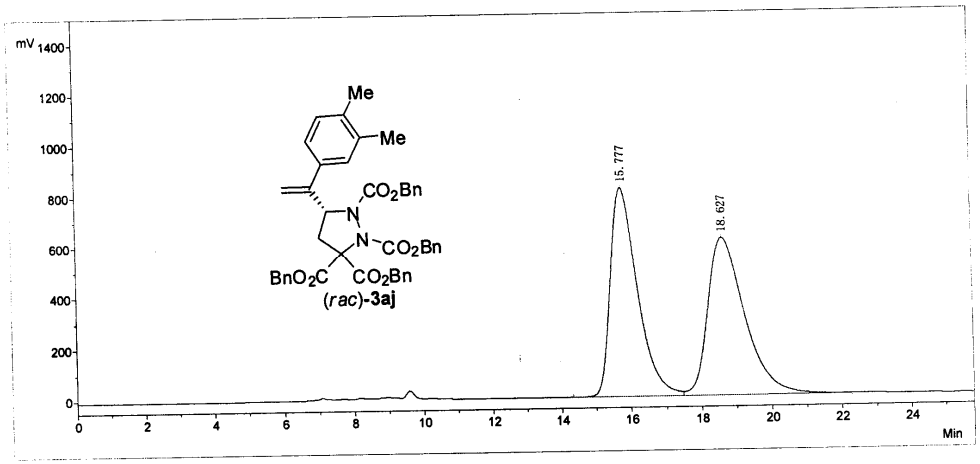

sw-10-101-c
167.816
166.039
157.078
153.323
143.493
136.570
136.325
136.042
135.626
135.410
134.919
134.518
129.654
128.427
128.383
128.346
128.271
128.175
128.137
128.100
128.063
127.952
127.728
127.624
123.966
112.723
77.320
77.000
76.688
72.226
68.456
68.263
68.144
68.017
61.310
41.463
19.772
19.386
Me
Me
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3aj
200
180
160
140
120
100
80
60
40
20
ppm


sw-10-101-C
128.427
128.383
128.346
128.271
128.175
128.137
128.100
128.063
127.952
127.728
127.624
Me
Me
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3aj
128.8
128.6
128.4
128.2
128.0
127.8
127.6
127.4
ppm

HPLC REPORT

Sample Name:sw-10-99rac od250 60 0.5.che
Time:09:12
column: OD-H (1")
Velocity: 0.5

Date:2009-01-14
Method:
the mobile phase: 60/40
the detection wavelength: 230

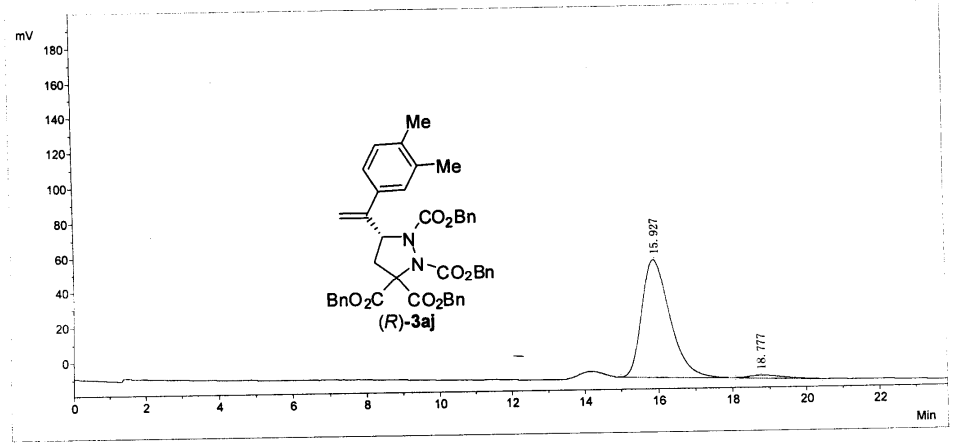


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	15.777	818096.4	43640266.3	49.5067
2	2	18.627	616244.8	44510018.9	50.4933
Total			1434341.2	88150285.2	100.0000

HPLC REPORT

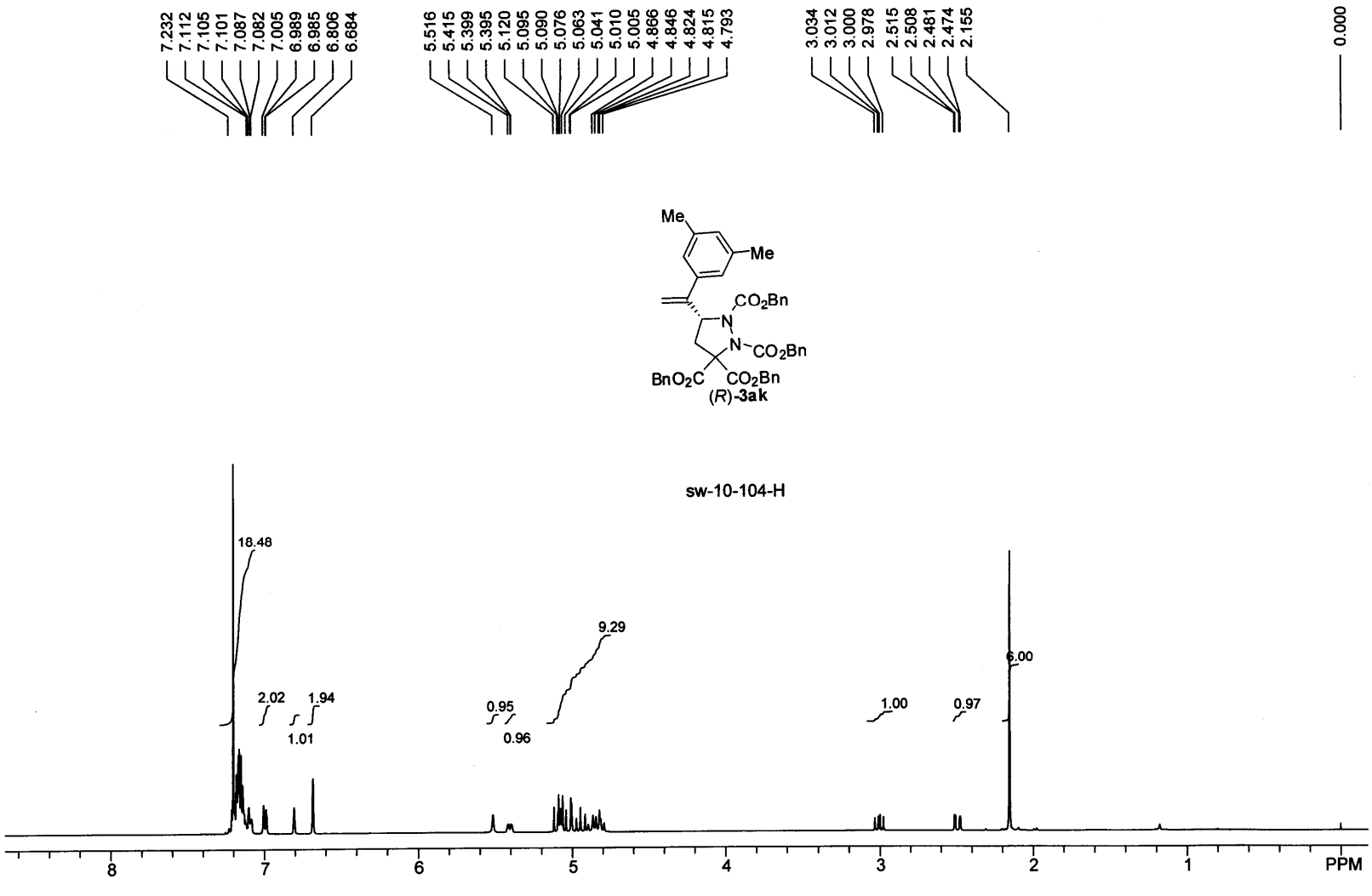
Sample Name:sw-10-101.che
Time:09:38
column:
Velocity:

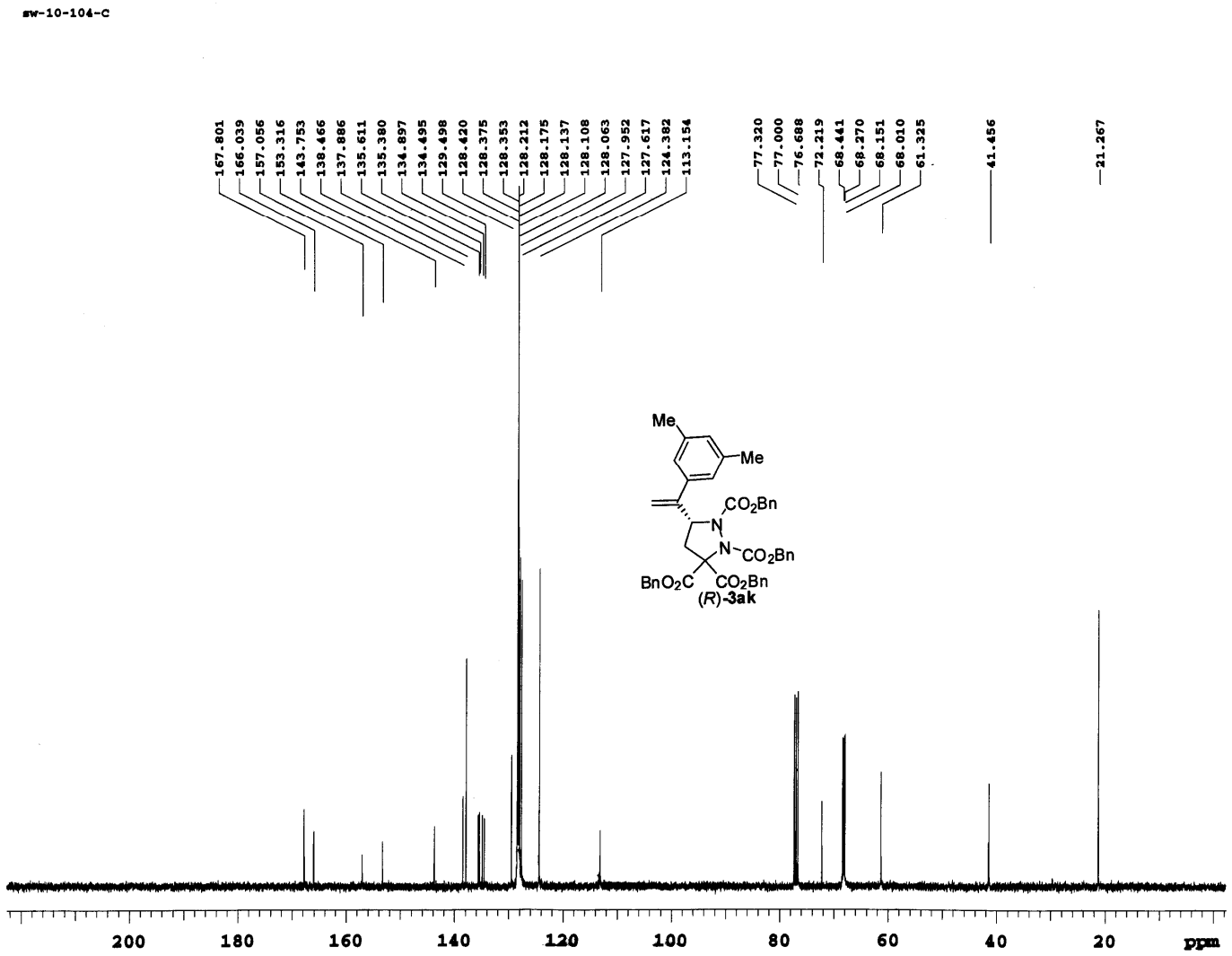
Date:2009-01-14
Method:
the mobile phase:
the detection wavelength:

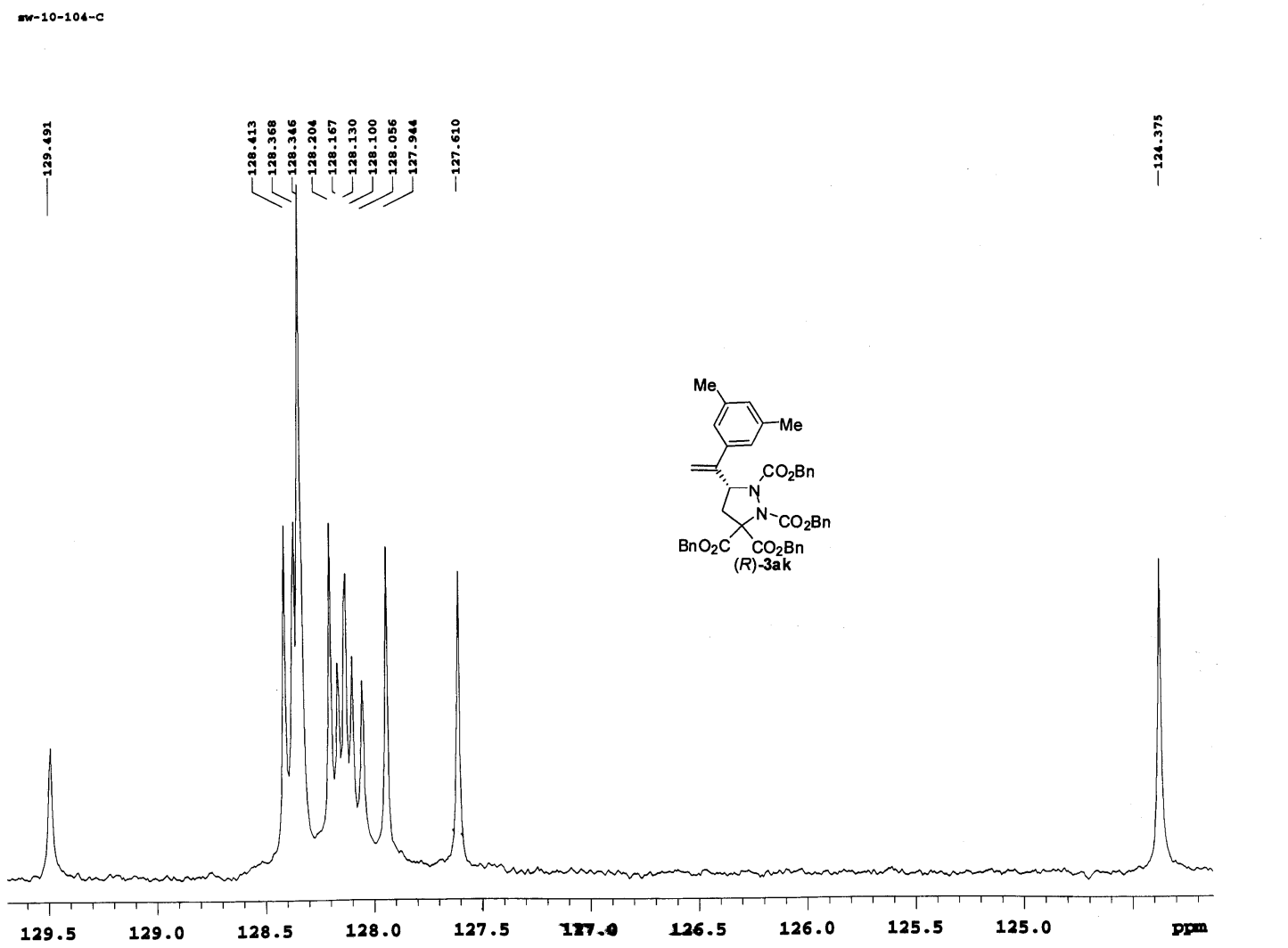


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	15.927	67339.5	3525397.7	97.5199
2	2	18.777	1457.6	89656.4	2.4801
Total			68797.0	3615054.1	100.0000

ee = 95.1%


7.232
7.112
7.105
7.101
7.087
7.082
7.005
6.989
6.985
6.806
6.684
5.516
5.415
5.399
5.395
5.120
5.095
5.090
5.076
5.063
5.041
5.010
5.005
4.866
4.846
4.824
4.815
4.793
3.034
3.012
3.000
2.978
2.515
2.508
2.481
2.474
2.155
0.000
Me
Me
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ak
sw-10-104-H
18.48
2.02
1.94
1.01
0.95
0.96
9.29
1.00
0.97
6.00
8
7
6
5
4
3
2
1
PPM

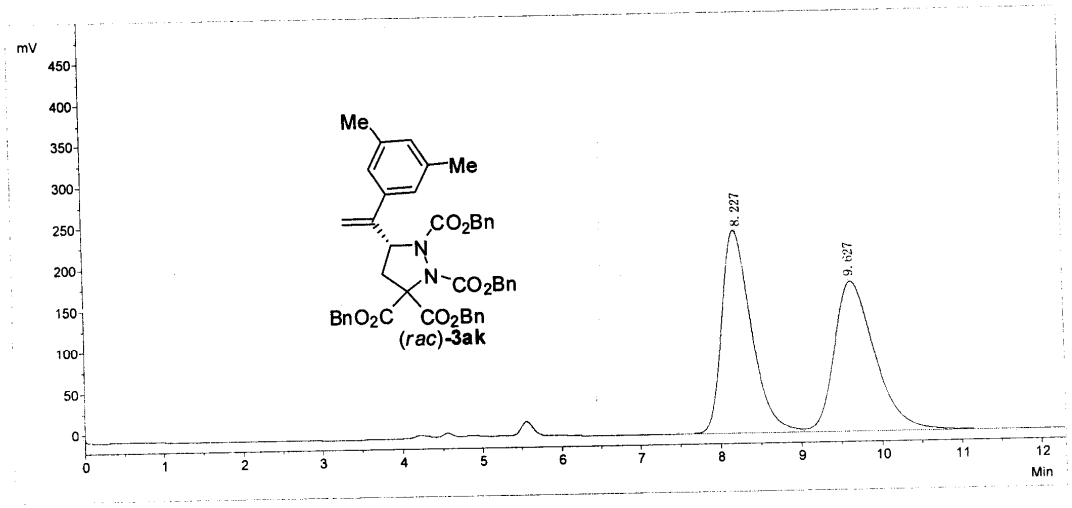

sw-10-104-C
167.801
166.039
157.056
153.316
143.753
138.466
137.886
135.611
135.380
134.897
134.495
129.498
128.420
128.375
128.353
128.212
128.175
128.137
128.108
128.063
127.952
127.617
124.382
113.154
77.320
77.000
76.688
72.219
68.441
68.270
68.151
68.010
61.325
41.456
21.267
Me
Me
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ak
200
180
160
140
120
100
80
60
40
20
ppm


sw-10-104-C
129.491
128.413
128.368
128.346
128.204
128.167
128.130
128.100
128.056
127.944
127.610
124.375
Me
Me
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3ak
129.5
129.0
128.5
128.0
127.5
126.5
126.0
125.5
125.0
ppm

HPLC REPORT

Sample Name:sw-10-105rac od 60 0.5.che
Time:15:37
column: OD-H
Velocity: 0.5

Date:2009-01-13
Method:
the mobile phase: 60/40
the detection wavelength: 230

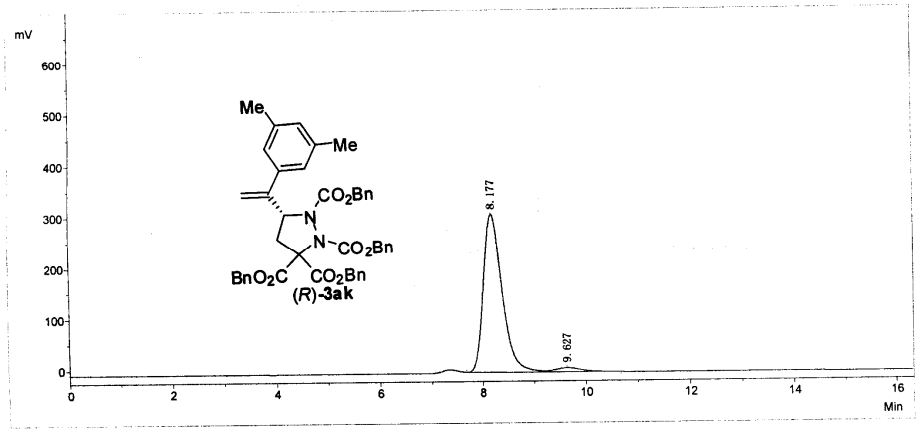


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	8.227	243289.9	6265045.4	49.6355
2	2	9.627	180486.0	6357070.4	50.3645
Total			423776.0	12622115.8	100.0000

HPLC REPORT

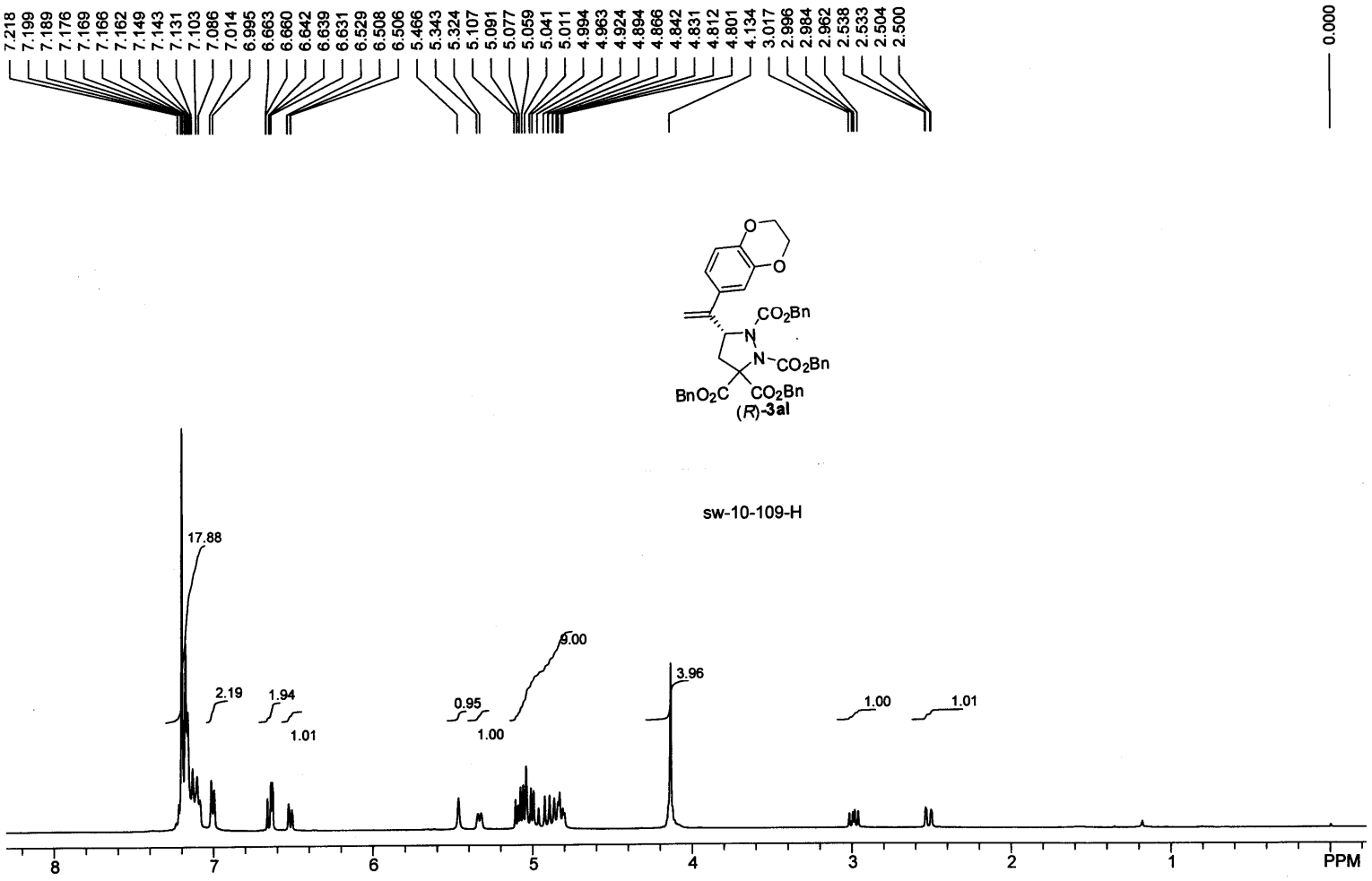
Sample Name:sw-10-104.che
Time:15:50
column:
Velocity:

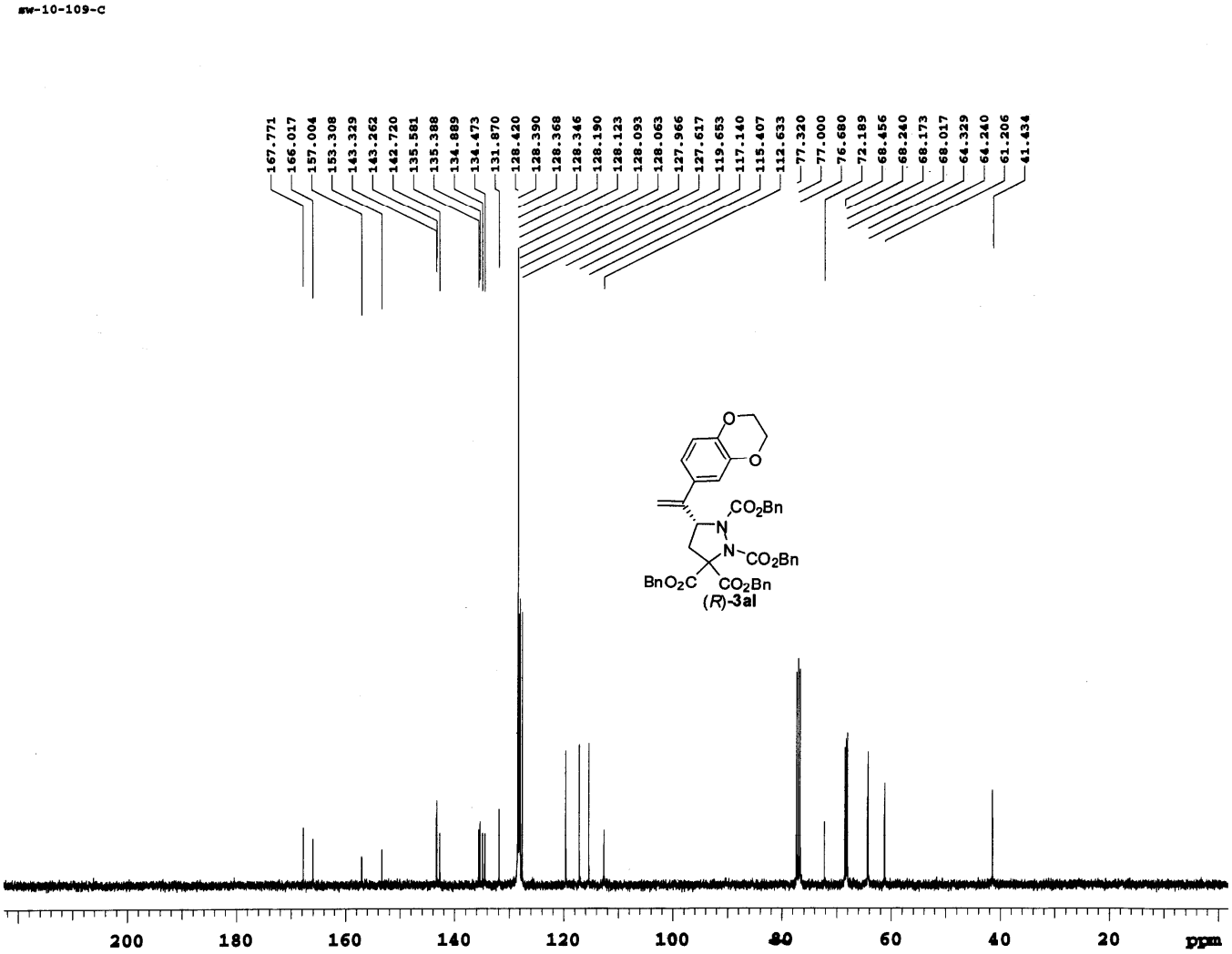
Date:2009-01-13
Method:
the mobile phase:
the detection wavelength:

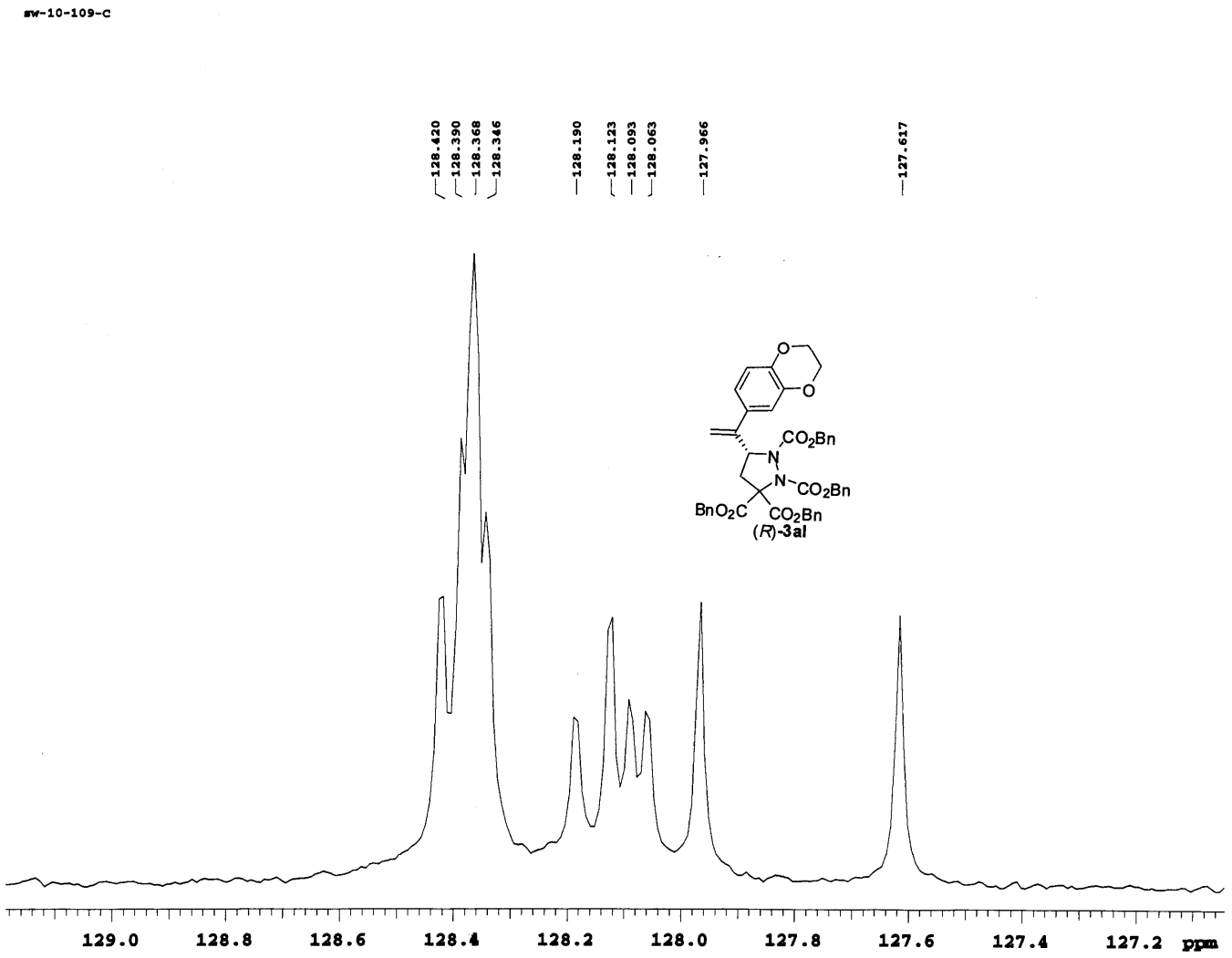


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	8.177	309178.4	7817829.9	96.5311
2	2	9.627	7830.7	280941.4	3.4689
Total			317009.1	8098771.3	100.0000

ee = 96.5311 − 3.4689
= 93.1%


7.218
7.199
7.189
7.176
7.169
7.166
7.162
7.149
7.143
7.131
7.103
7.086
7.014
6.995
6.663
6.660
6.642
6.639
6.631
6.529
6.508
6.506
5.466
5.343
5.324
5.107
5.091
5.077
5.059
5.041
5.011
4.994
4.963
4.924
4.894
4.866
4.842
4.831
4.812
4.801
4.134
3.017
2.996
2.984
2.962
2.538
2.533
2.504
2.500
0.000
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3al
sw-10-109-H
17.88
2.19
1.94
1.01
0.95
1.00
9.00
3.96
1.00
1.01
8
7
6
5
4
3
2
1
PPM

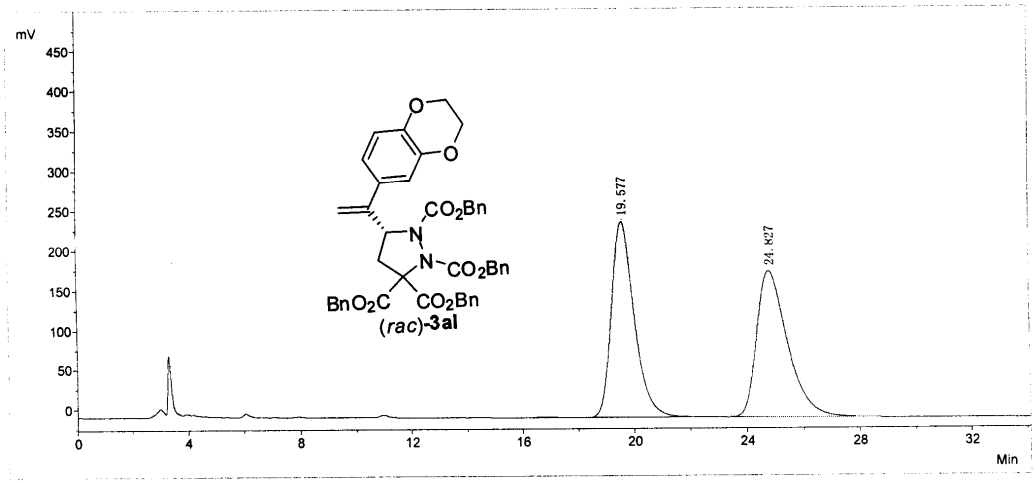

sw-10-109-c
167.771
166.017
157.004
153.308
143.329
143.262
142.720
135.581
135.388
134.889
134.473
131.870
128.420
128.390
128.368
128.346
128.190
128.123
128.093
128.063
127.966
127.617
119.653
117.140
115.407
112.633
77.320
77.000
76.680
72.189
68.456
68.240
68.173
68.017
64.329
64.240
61.206
41.434
O
O
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3al
200
180
160
140
120
100
80
60
40
20
ppm


sw-10-109-C
128.420
128.390
128.368
128.346
128.190
128.123
128.093
128.063
127.966
127.617
CO2Bn
CO2Bn
BnO2C
CO2Bn
(R)-3al
129.0
128.8
128.6
128.4
128.2
128.0
127.8
127.6
127.4
127.2
ppm

HPLC REPORT

Sample Name:sw-10-107rac ad 60.che
Time:11:19
column: AD-H
Velocity: 0.7

Date:2009-01-16
Method:
the mobile phase: 60/40
the detection wavelength: 230

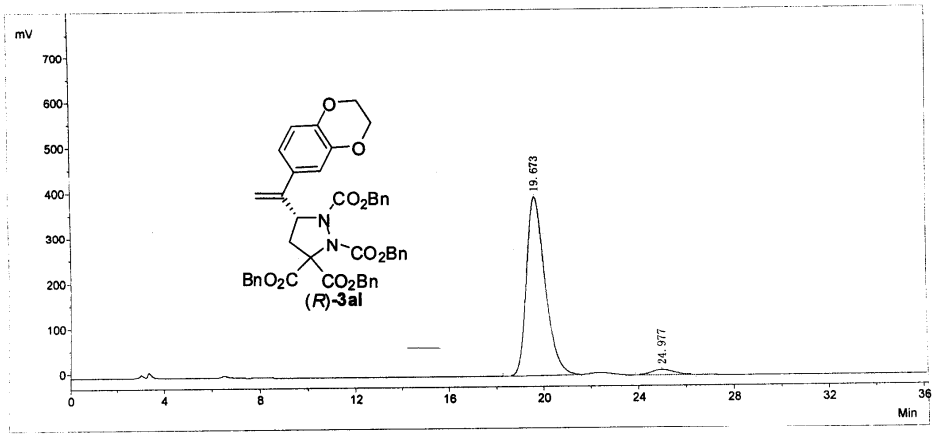


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	19.577	244991.3	13852002.5	49.9011
2	2	24.827	183442.6	13906900.4	50.0989
Total			428433.8	27758902.9	100.0000

HPLC REPORT

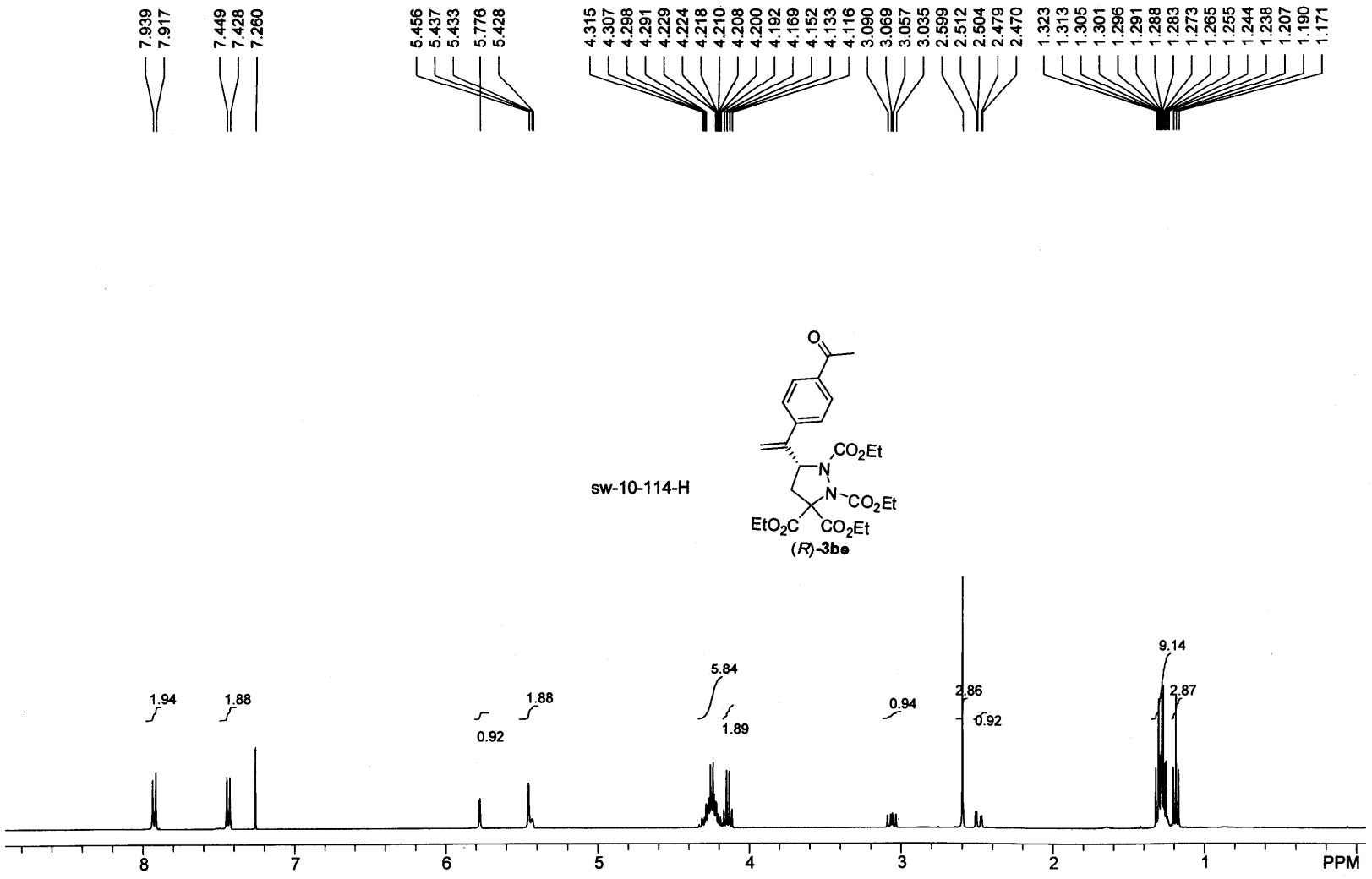
Sample Name:sw-10-109.che
Time:11:54
column:
Velocity:

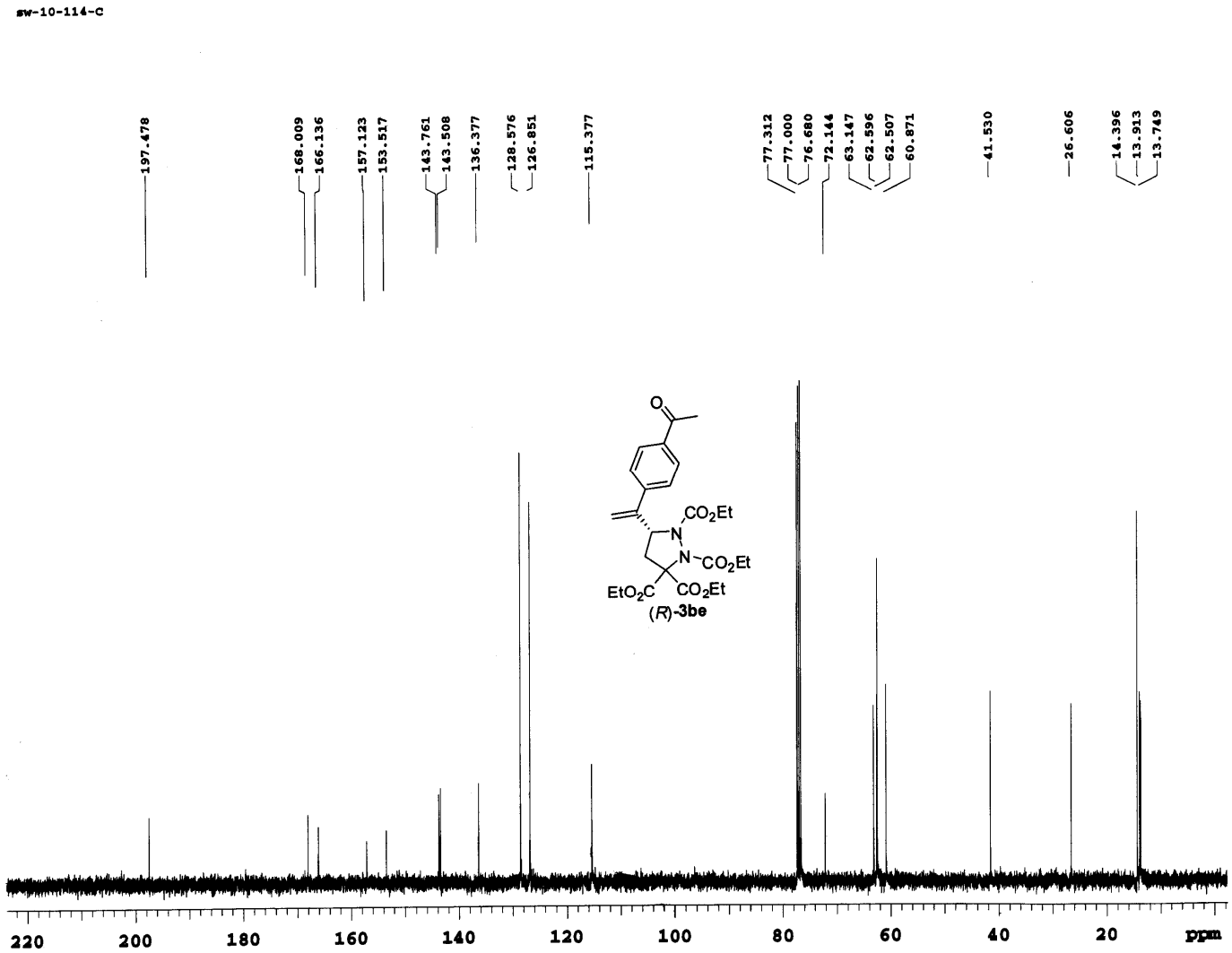
Date:2009-01-16
Method:
the mobile phase:
the detection wavelength:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	19.673	393929.4	21603452.5	96.6284
2	2	24.977	11485.8	753807.3	3.3716
Total			405415.2	22357259.8	100.0000

ee = 93.2%

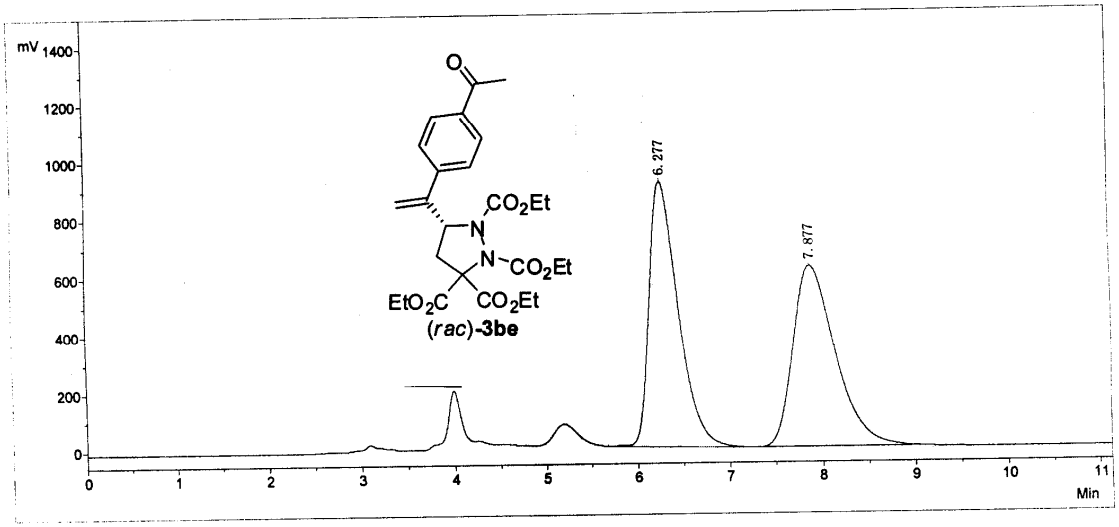

7.939
7.917
7.449
7.428
7.260
5.456
5.437
5.433
5.776
5.428
4.315
4.307
4.298
4.291
4.229
4.224
4.218
4.210
4.208
4.200
4.192
4.169
4.152
4.133
4.116
3.090
3.069
3.057
3.035
2.599
2.512
2.504
2.479
2.470
1.323
1.313
1.305
1.301
1.296
1.291
1.288
1.283
1.273
1.265
1.255
1.244
1.238
1.207
1.190
1.171
sw-10-114-H
CO2Et
N
N
CO2Et
EtO2C
CO2Et
(R)-3be
1.94
1.88
0.92
1.88
5.84
1.89
0.94
2.86
0.92
9.14
2.87
8
7
6
5
4
3
2
1
PPM


sw-10-114-C
197.478
168.009
166.136
157.123
153.517
143.761
143.508
136.377
128.576
126.851
115.377
77.312
77.000
76.680
72.144
63.147
62.596
62.507
60.871
41.530
26.606
14.396
13.913
13.749
O
CO2Et
N
N
CO2Et
EtO2C
CO2Et
(R)-3be
220
200
180
160
140
120
100
80
60
40
20
ppm

HPLC REPORT

Sample Name:sw-10-103rac od 60.che
Time:10:09
column: OD-H
Velocity: 0.7

Date:2009-01-16
Method:
the mobile phase: 60/40
the detection wavelength: 214

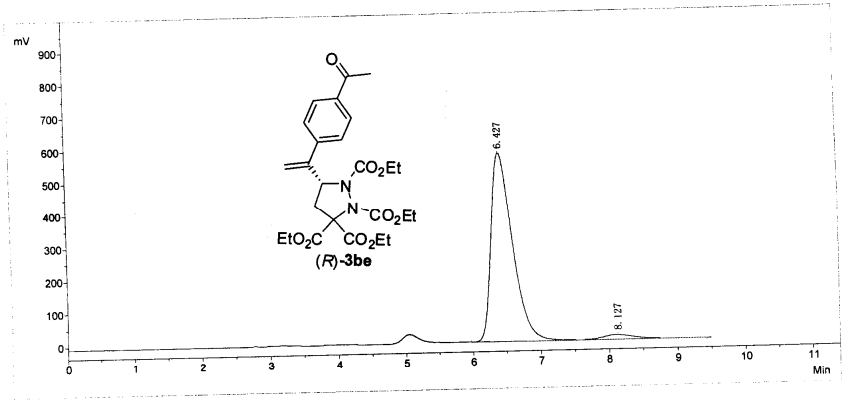


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	6.277	913565.4	19980125.3	50.1850
2	2	7.877	626512.0	19832831.4	49.8150
Total			1540077.3	39812956.7	100.0000

HPLC REPORT

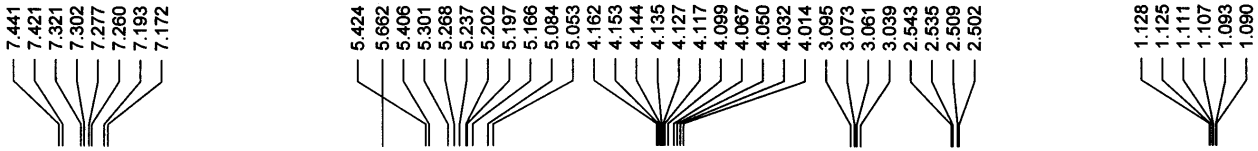
Sample Name:sw-10-114.che
Time:10:21
column:
Velocity:

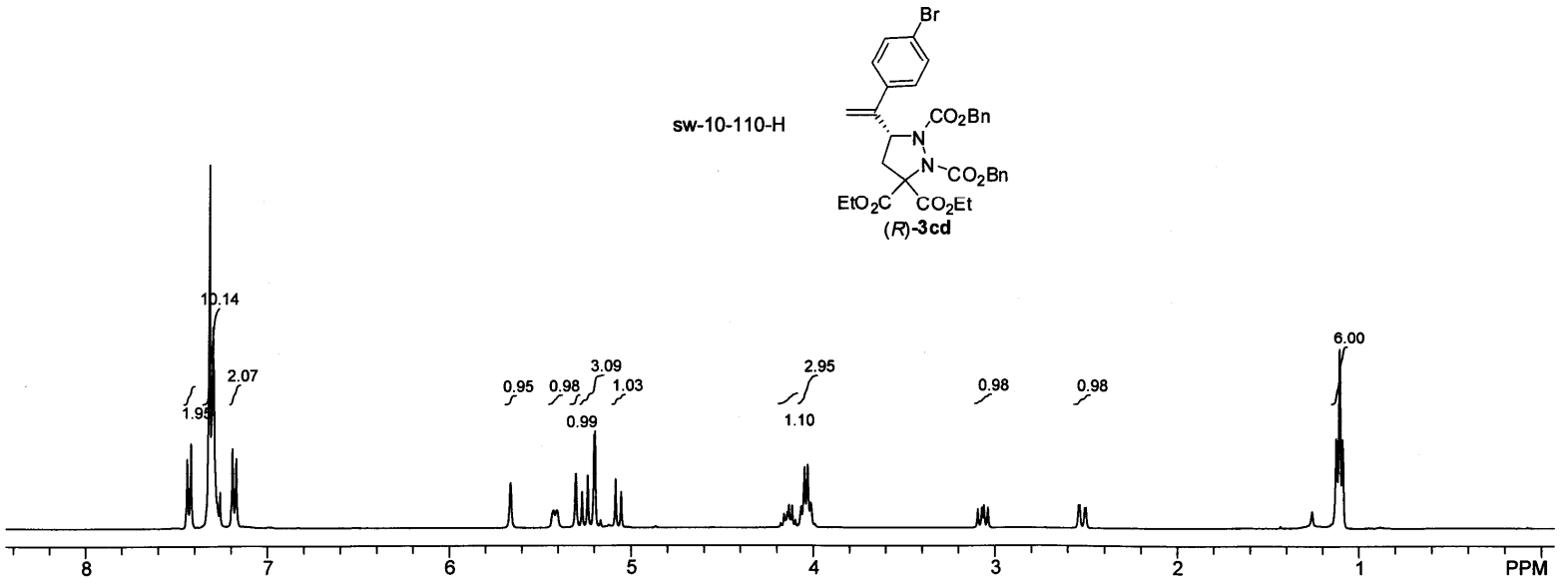
Date:2009-01-16
Method:
the mobile phase:
the detection wavelength:

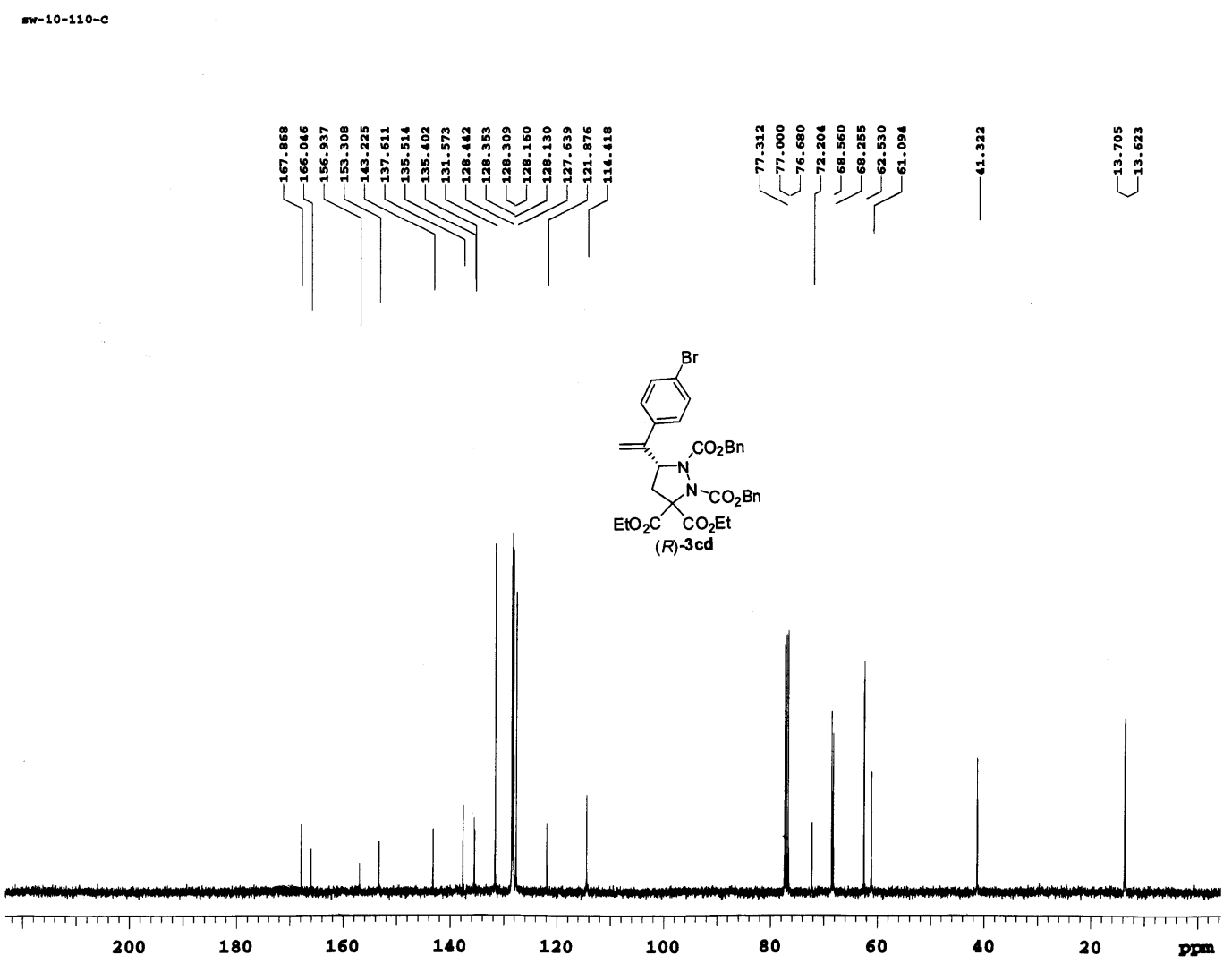


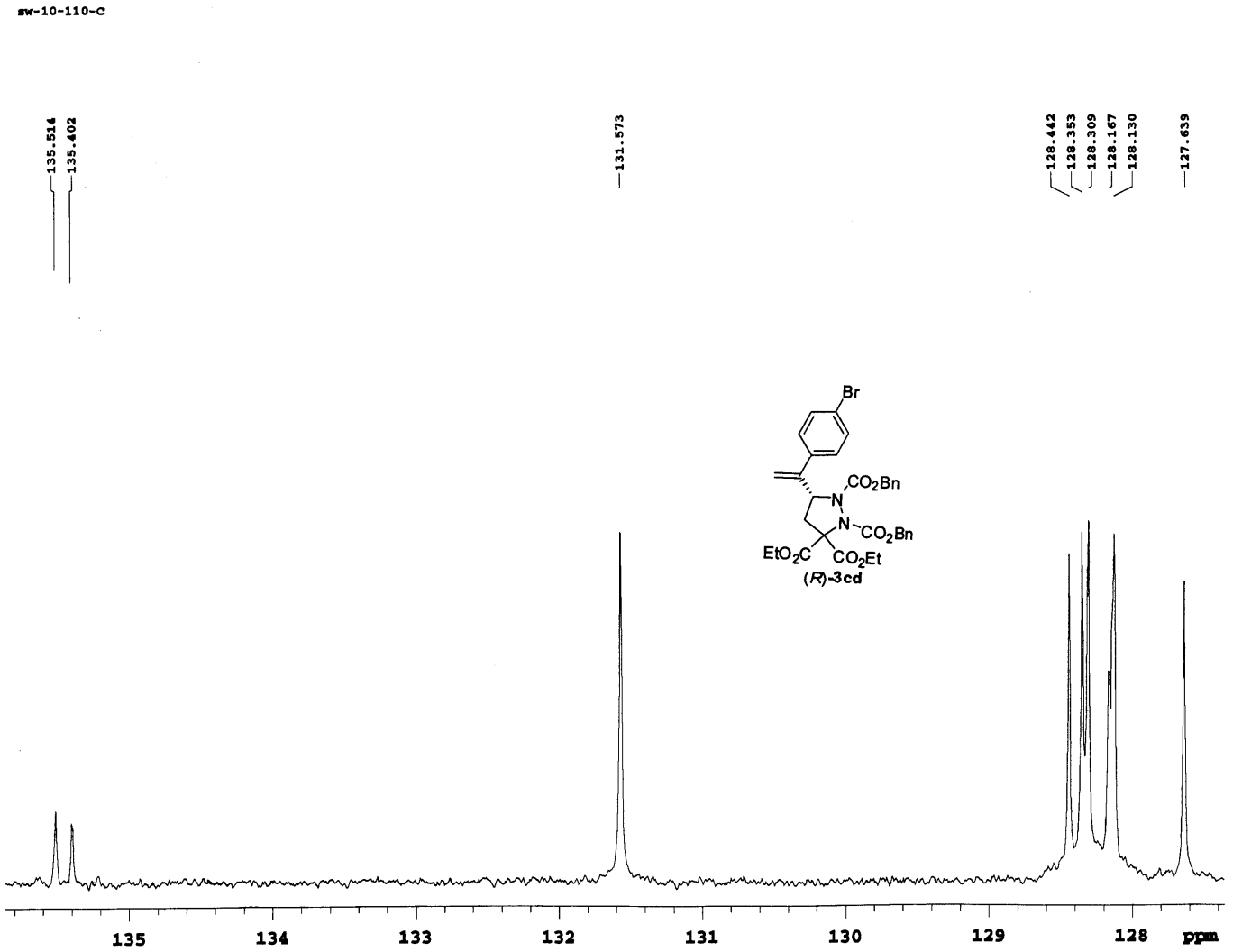
No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	6.427	575933.7	12643572.2	96.5410
2	2	8.127	13937.0	453014.7	3.4590
Total			589870.7	13096586.9	100.0000

ee = 93.1%


7.441
7.421
7.321
7.302
7.277
7.260
7.193
7.172
5.424
5.662
5.406
5.301
5.268
5.237
5.202
5.197
5.166
5.084
5.053
4.162
4.153
4.144
4.135
4.127
4.117
4.099
4.067
4.050
4.032
4.014
3.095
3.073
3.061
3.039
2.543
2.535
2.509
2.502
1.128
1.125
1.111
1.107
1.093
1.090


sw-10-110-H
Br
CO2Bn
N
N
CO2Bn
EtO2C
CO2Et
(R)-3cd
10.14
2.07
1.95
0.95
0.98
3.09
0.99
1.03
2.95
1.10
0.98
0.98
6.00
8
7
6
5
4
3
2
1
PPM

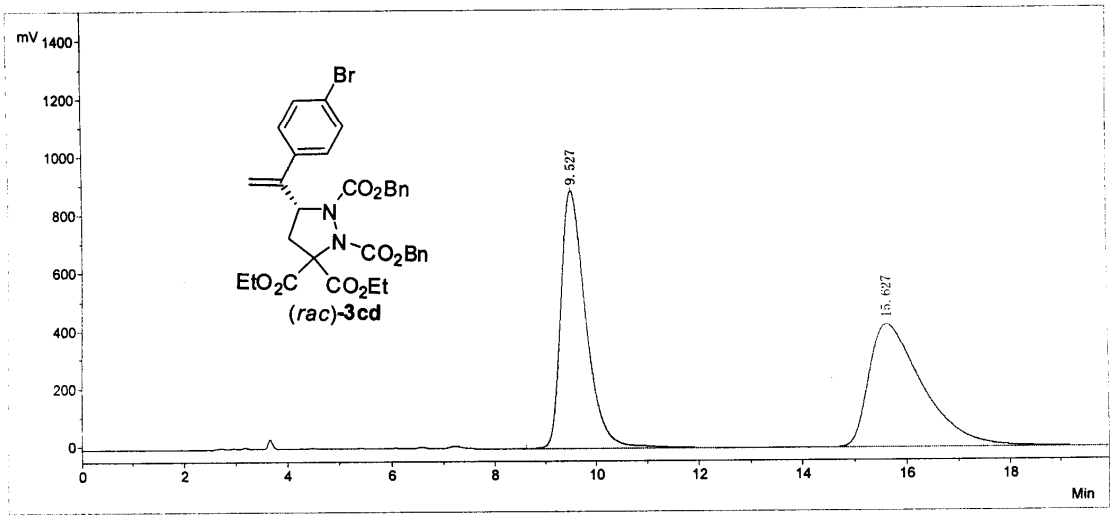

sw-10-110-c
167.868
166.046
156.937
153.308
143.225
137.611
135.514
135.402
131.573
128.442
128.353
128.309
128.160
128.130
127.639
121.876
114.418
77.312
77.000
76.680
72.204
68.560
68.255
62.530
61.094
41.322
13.705
13.623
Br
CO2Bn
N
N
CO2Bn
EtO2C
CO2Et
(R)-3cd
200
180
160
140
120
100
80
60
40
20
ppm


sw-10-110-c
135.514
135.402
131.573
128.442
128.353
128.309
128.167
128.130
127.639
Br
CO2Bn
N
N
CO2Bn
EtO2C
CO2Et
(R)-3cd
135
134
133
132
131
130
129
128
ppm

HPLC REPORT

Sample Name:sw-3-184rac od 85.che
Time:13:28
column: OD-H
Velocity: 0.7

Date:2009-01-16
Method:
the mobile phase: 85/15
the detection wavelength: 230

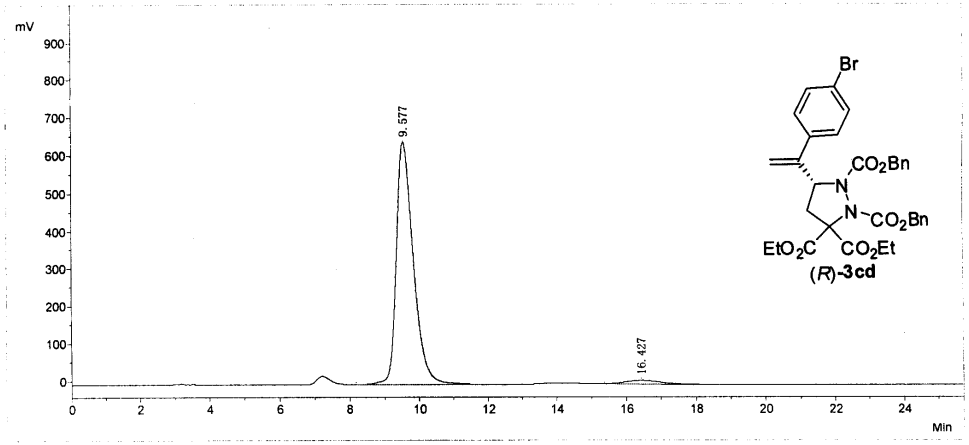


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	9.527	886926.7	30045903.7	49.8463
2	2	15.627	423436.4	30231147.0	50.1537
Total			1310363.1	60277050.7	100.0000

HPLC REPORT

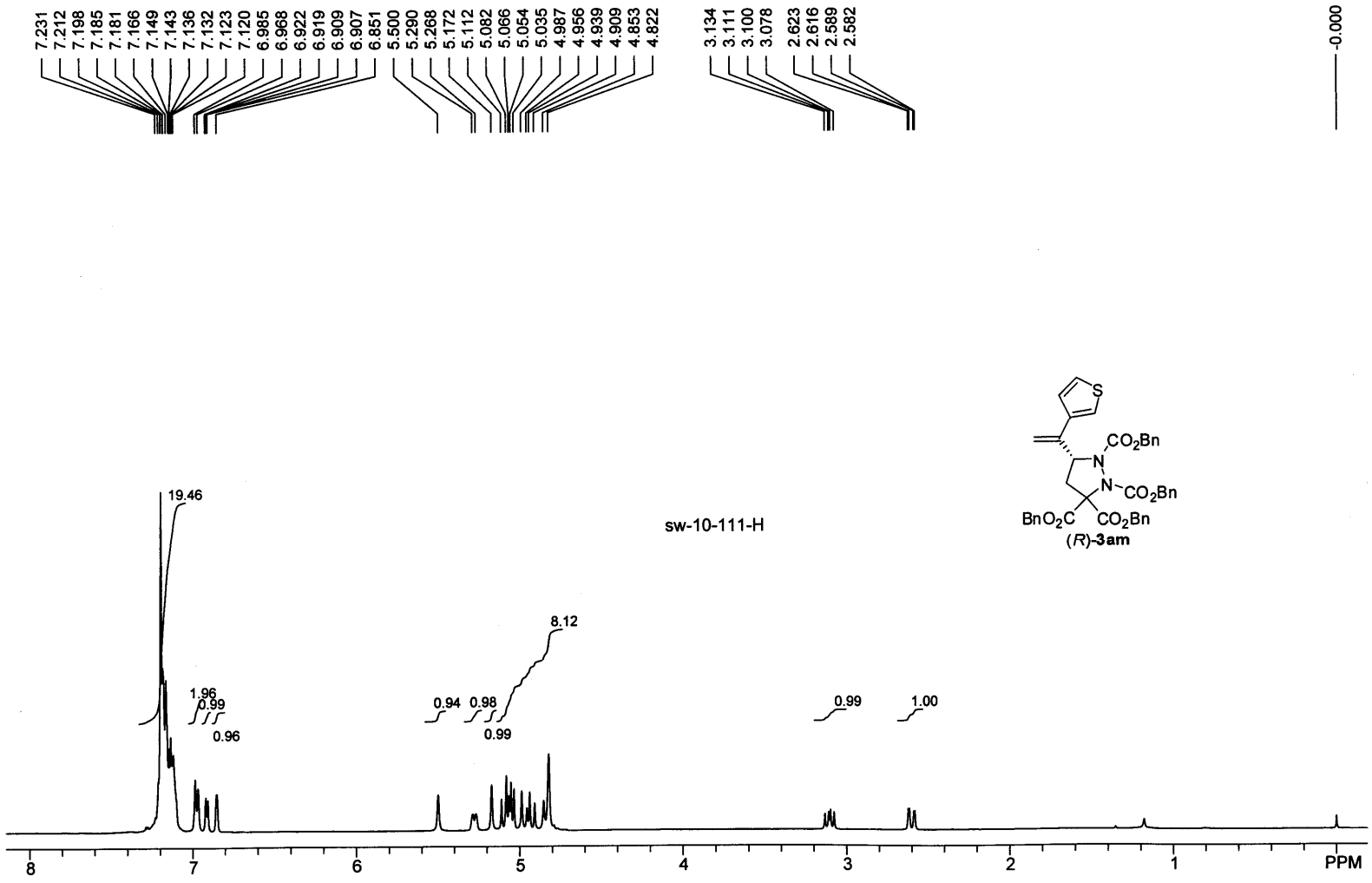
Sample Name:sw-10-110.che
Time:13:48
column:
Velocity:

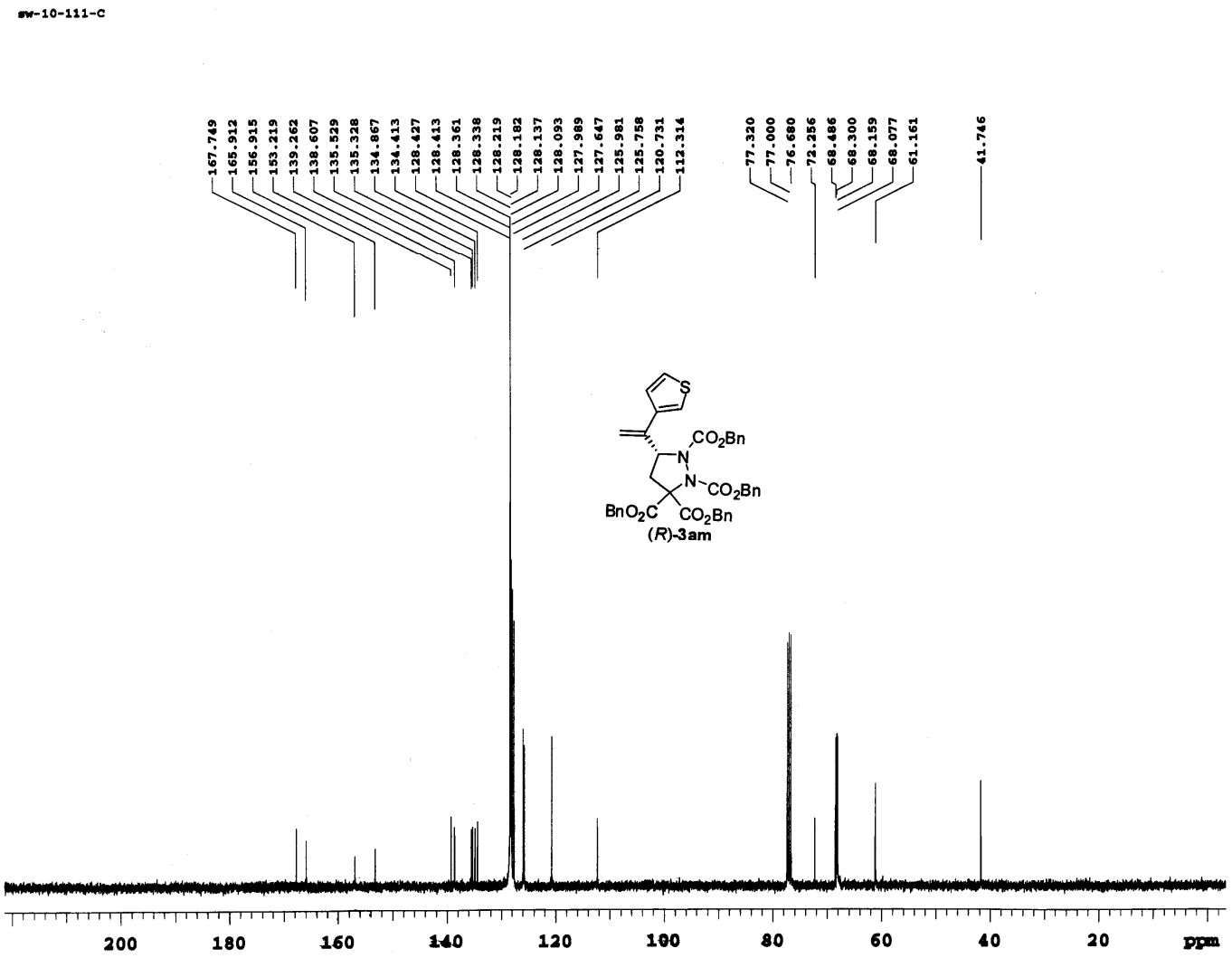
Date:2009-01-16
Method:
the mobile phase:
the detection wavelength:

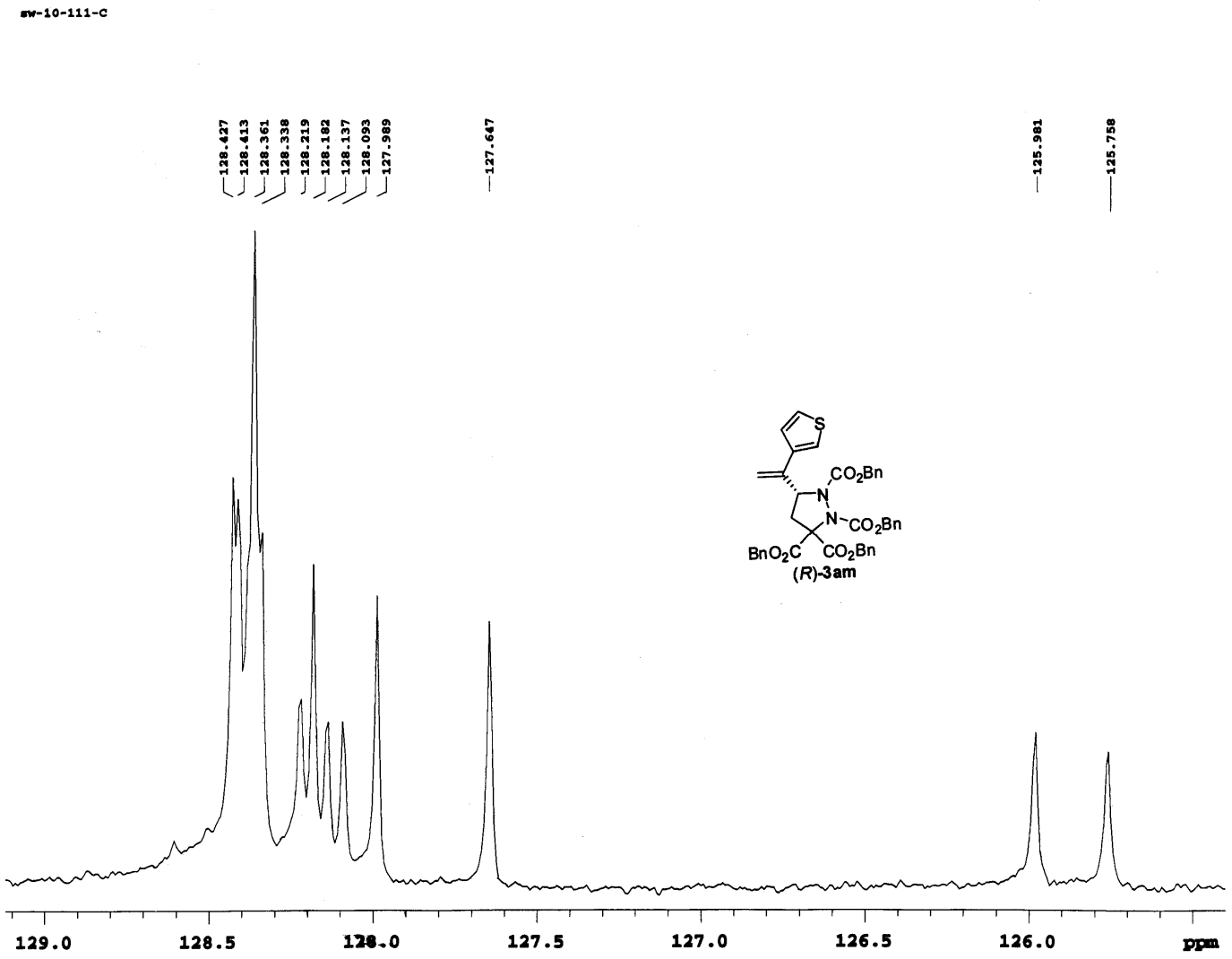


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	9.577	642661.3	22136518.3	97.4121
2	2	16.427	8756.0	588094.7	2.5879
Total			651417.3	22724613.0	100.0000

ee = 94.8%


7.231
7.212
7.198
7.185
7.181
7.166
7.149
7.143
7.136
7.132
7.123
7.120
6.985
6.968
6.922
6.919
6.909
6.907
6.851
5.500
5.290
5.268
5.172
5.112
5.082
5.066
5.054
5.035
4.987
4.956
4.939
4.909
4.853
4.822
3.134
3.111
3.100
3.078
2.623
2.616
2.589
2.582
-0.000
sw-10-111-H
19.46
1.96
0.99
0.96
0.94
0.98
0.99
8.12
0.99
1.00
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3am
8
7
6
5
4
3
2
1
PPM

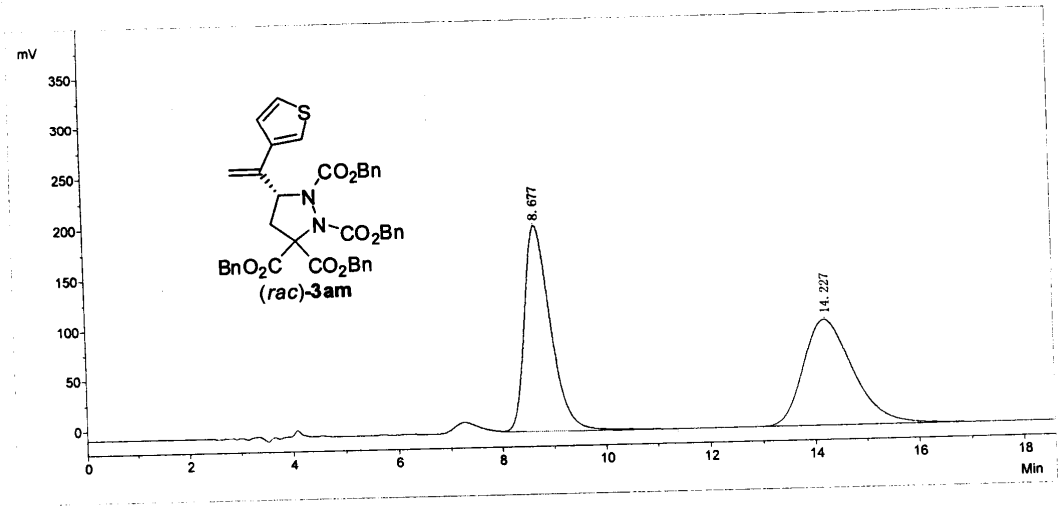

sw-10-111-c
167.749
165.912
156.915
153.219
139.262
138.607
135.529
135.328
134.867
134.413
128.427
128.413
128.361
128.338
128.219
128.182
128.137
128.093
127.989
127.647
125.981
125.758
120.731
112.314
77.320
77.000
76.680
72.256
68.486
68.300
68.159
68.077
61.161
41.746
S
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3am
200
180
160
140
120
100
80
60
40
20
ppm


sw-10-111-C
128.427
128.413
128.361
128.338
128.219
128.182
128.137
128.093
127.989
127.647
125.981
125.758
S
CO2Bn
N
N
CO2Bn
BnO2C
CO2Bn
(R)-3am
129.0
128.5
128.0
127.5
127.0
126.5
126.0
ppm

HPLC REPORT

Sample Name:sw-10-108rac od 60 214.che
Time:09:07
column: ODH
Velocity: 0.7

Date:2009-01-16
Method:
the mobile phase: 60/40
the detection wavelength: 214

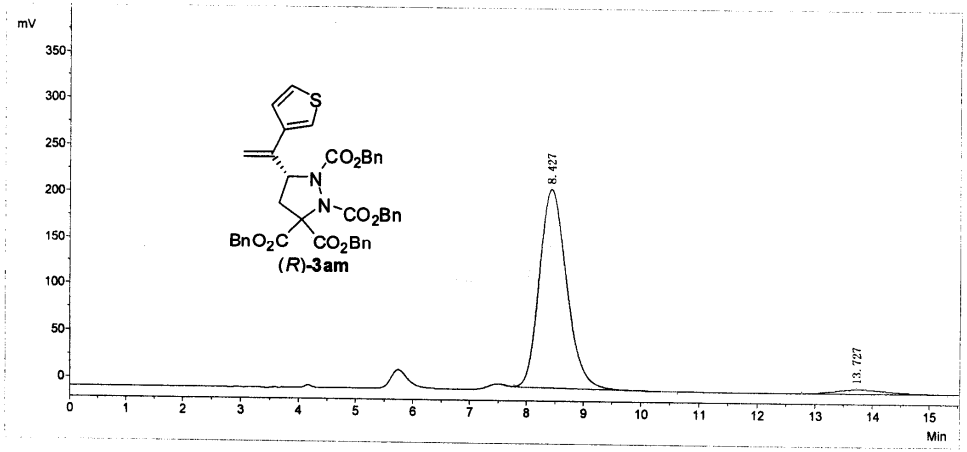


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	8.677	202887.5	7077607.9	50.3685
2	2	14.227	105336.0	6974034.6	49.6315
Total			308223.5	14051642.5	100.0000

HPLC REPORT

Sample Name:sw-10-111.che
Time:09:27
column:
Velocity:

Date:2009-01-16
Method:
the mobile phase:
the detection wavelength:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	8.427	212444.5	6998903.3	96.2023
2	2	13.727	4450.0	276290.3	3.7977
Total			216894.4	7275193.6	100.0000

ee = 92.4%