Supporting Information for the Communication entitled

Enantioselective Synthesis of "Quaternary" 1,4-Benzodiazepine-2-ones via Memory of Chirality

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Table of Contents:

A. Experimental Procedures

General

THF was distilled from Na/benzophenone immediately before use. (*S*)-Boc-Ala and (*S*)-Boc-Phe were purchased from Advanced ChemTech and were used as received. Compounds **1a** and **1b** were prepared according to the literature method.[1] Compounds (*3S*)-**2a** and (*3S*)-**3a** were prepared in 91 and 67% yield from (*S*)-Boc-Ala and (*S*)-Boc-Phe using a modification of Shea's protocol;[2] enantiomeric excess of these compounds was assessed by HPLC (Chiralcel AD and OD). Isopropyl triflate was prepared according to the literature[3] immediately before use and was dispensed as a solution in CCl_4. ^{1}H NMR Spectra were recorded at 500 and 400 MHz; the

corresponding ^{13}C NMR resonant frequencies were 125 and 100 MHz respectively. High resolution mass spectra were recorded under FAB conditions (NBA. PEG); in each case the expected molecular formula (M+1, ^{35}Cl) gave the closest match among all possible formulas.

General procedure for *N*-alkylation of *N-H*-1,4-benzodiazepine-2-ones

At 0 °C to a stirred solution of (*3S*)-**2a** (5.1 mmol, 1.0 equiv.) in dry THF (30.0 mL) was added NaH (5.7 mmol, 1.12 equiv., 60% suspension in mineral oil) in one portion. The resulting solution was stirred at 0 °C for 30 min before the dropwise addition of alkyl triflate (15 mmol, 3.0 equiv.). The reaction mixture was stirred for a further 10 min at 0 °C, at which point TLC (1:5 EtOAc:hexanes) indicated the reaction was complete. The reaction was quenched at 0 °C with 20 ml of saturated aqueous NH_4Cl solution, and extracted with CH_2Cl_2 (3 x 30 mL). The combined extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel.

***N-i*-Pr benzodiazepine 1c**

The procedure above was followed with **1a** (102 mg, 0.376 mmol) in anhydrous THF (2 mL), HMPA (390 μL, 2.26 mmol), NaH (0.451 mmol), *i*-PrOTs (241.7 mg, 1.13 mmol). After stirring overnight, aqueous workup and chromatography (20% EtOAc/Hexane) afforded 65.2 mg (55%) of **1c** as a yellow oil.

^1H NMR ($CDCl_3$) δ 1.21 (d, *J* = 7.1 Hz, 3H), 1.50 (d, *J* = 6.7 Hz, 3H), 3.73 (d, *J* = 10.5 Hz, 1H), 4.55 (m, *J* = 6.9 Hz, 1H), 4.75 (d, *J* = 10.5 Hz, 1H), 7.27 (s, 1H), 7.37-7.50 (m, 5H), 7.61 (m, 1H);

^{13}C NMR ($CDCl_3$) δ 20.62, 22.39, 51.08, 58.05, 125.23, 128.59, 129.31, 129.55, 130.42, 130.72, 130.76, 132.44, 138.16, 140.72, 168.68, 169.52;

HRMS (FAB) calcd for $C_{18}H_{18}N_2OCl$ $[M + H]^+$ 313.1108, found 313.1123 (+4.8 ppm, +1.5 mmu)

***N*-Me benzodiazepine (*3S*)-2b**

The procedure above was followed with (*3S*)-**2a** (0.12g, 0.42 mmol) in anhydrous THF (2.0 mL), 60% NaH (19 mg, 0.47 mmol) and methyl triflate (58μL, 0.51mmol). Purification with flash column chromatography on silica gel (1:2 Hexanes/EtOAc) provided 118 mg (94%) of (*3S*)-**2b**, which was identical by ^1H NMR to the literature material.[4] Chiral stationary phase HPLC (Chiralcel AD) indicated 100 %ee.

***N-i*-Pr benzodiazepine (*3S*)-2c**

The procedure above was followed with (*3S*)-**2a** (1.44 g, 5.08 mmol) in anhydrous THF (30.0 ml), 60% NaH (228.0 mg, 5.69 mmol) and isopropyl triflate (2.92 g, 15.2 mmol, solution in 2 mL CCl_4). Purification with flash column chromatography on silica gel (1:5 Hexanes/EtOAc) provided 1.36 g (82%) of (*3S*)-**2c** as a white solid, mp 113.8 –114.9 °C.

^1H NMR ($CDCl_3$): δ 7.61-7.58 (m, 2H), 7.48-7.35 (m, 5H), 7.25 (s, 1H), 4.55 (septet, *J* = 6.9 Hz, 1H), 3.67 (q, *J* = 6.4 Hz, 1H), 1.69 (d, *J* = 6.4 Hz, 3H), 1.48 (d, *J* = 6.9 Hz, 3H), 1.20 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$): δ 170.8, 166.6, 140.4, 138.1, 133.0, 130.64, 130.58, 130.3, 129.4, 129.3, 128.6, 125.3, 59.7, 51.4, 22.3, 20.7, 17.3.

HRMS calcd. for $C_{19}H_{20}ClN_2O$ (M+1) 327.1264, found 327.1264.

$[\alpha]^{21}_D$= +222.7° (c = 0.55, $CHCl_3$). Chiral stationary phase HPLC (Chiralcel AD) indicated 100 %ee.

***N*-*i*-Pr Benzodiazepine (*3S*)-3c**

The procedure above was followed with (*3S*)-**3a** (0.683 g, 1.89 mmol) in anhydrous THF (14 mL), 60% NaH (84.7 mg, 2.12 mmol) and isopropyl triflate (1.0921g, 5.68 mmol (neat)). Purification with flash column chromatography on silica gel (1:4 EtOAc:hexanes) provided 0.439 g (58%) of (*3S*)-**3c** as a pale yellow solid, mp 67-69 °C.

^{1}H NMR ($CDCl_3$): □ 7.56-7.15 (several multiplets, 13H), 4.58 (septet, *J* = 6.9 Hz, 1H), 3.70 (dd, *J* = 8.2, 5.4 Hz, 1H), 3.586 (dd, *J* = 13.9, 8.2 Hz, 1H), 3.525 (dd, *J* = 13.9, 5.4 Hz, 1H), 1.56 (s, 3H), 1.47 (d, *J* = 6.7 Hz, 3H), 1.19 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$): 169.8, 166.8, 140.2, 139.5, 138.1, 132.7, 130.66, 130.62, 130.4, 129.9, 129.39, 129.33, 128.5, 128.2, 126.1, 125.4, 66.0, 51.5, 37.8, 22.3, 20.6.

HRMS: calcd for $C_{25}H_{23}N_2OCl$ (M+1) 403.1577, found 403.1583 (+1.4 ppm, +0.6 mmu).

$[\square]^{21}_D$= +64.4° (c = 0.5, $CHCl_3$). Chiral stationary phase HPLC (Chiralcel AD) indicated 100 %ee.

General Protocol for the C3-alkylation of 3-alkyl-1,4-benzodiazepine-2-ones.

At –78 °C under nitrogen, to a stirred solution of (*3S*)-**2c** (0.15mmol, 1.0 equiv) and HMPA (0.90 mmol, 6.0 equiv) in anhydrous THF (3.0 mL) was added LDA (0.15 mmol, 1.2 equiv, 1.5 M in hexanes). After 15 minutes, *n*-BuLi (0.15 mmol, 1.2 equiv, 2.5 M in hexanes) was added and the mixture stirred for a further 15 min. The electrophile (1.5 mmol, 10 equiv.) was then added dropwise via syringe at –78 °C and the reaction was stirred at –78 °C until the starting benzodiazepine was consumed (TLC). The reaction was quenched at –78 °C by the addition of saturated aqueous NH_4Cl (5.0 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel.

***N*-Me Benzodiazepine benzylation product (±)-4**

The procedure above was followed with (*3S*)-**2b** (44.0 mg, 0.15mmol), HMPA (155 □L, 0.90 mmol), LDA (118 □L, 0.18 mmol, 1.5M in hexanes), *n*-BuLi (71.0 □L, 0.18 mmol, 2.5M in hexanes) and benzyl bromide (176.8 □L, 1.5 mmol). The reaction mixture was stirred at –78 °C for 3 h. Purification with flash column chromatography on silica gel (1:5 Hexanes/EtOAc) provided 37.5 mg (72%) of (±)-**4** as a colorless oil.

^{1}H NMR ($CDCl_3$) indicated a 56:44 mixture of the axial-Me and equatorial-Me conformers: □ 7.6-7.1 (m, 12H), 6.85 (br d, *J* = 6.0 Hz, 1H), 3.71 (d, *J* = 13.5, 1H □ 0.56 ax-Me), 3.48 (s, 3H □ 0.44 eq-Me), 3.46 (s, 3H □ 0.56 ax-Me, overlapping with signal at 3.48), 3.28 (d, *J* = 13.3, 1H □ 0.56 ax-Me) 2.58 (d, *J* = 13.5 Hz, 1H x 0.44 eq-Me), 2.52 (d, *J* = 13.5 Hz, 1H x 0.44 eq-Me), 1.75 (s, 3H □ 0.44 eq-Me), 0.79 (s, 3H □ 0.56 ax-Me)

^{3}C NMR ($CDCl_3$) was consistent with an approximate 1:1 mixture of axial-Me and equatorial-Me conformers (35 resonances found for a possible 2 x 20 unique carbons): 173.9, 172.9, 165.5, 164.9, 142.4, 139.9, 138.4, 136.6, 132.3, 131.8 (2 partially resolved peaks), 131.7, 131.5, 130.4, 129.9, 129.8, 129.5, 128.9, 128.7, 128.5, 128.33, 128.26, 127.5, 126.7, 126.3, 122.4, 122.2, 67.9, 65.8, 47.7, 37.7 (2 partially resolved peaks), 37.5, 28.3, 17.6 ;

HRMS calcd. for $C_{24}H_{22}ClN_2O$ (M+1) 389.1421, found 389.1419.

Chiral stationary phase HPLC (Chiralcel AD-H) indicated 0 %ee.

(*3R*)-5 from Ala-derived benzodiazepine (*3S*)-2c

The general procedure was followed with (*3S*)-**2c** (16.6 mg, 0.05mmol), HMPA (53.4 □l, 0.30 mmol), LDA (41 □L, 0.06 mmol, 1.5M in hexanes), *n*-BuLi (25 □L, 0.06 mmol, 2.5M in hexanes) and benzyl bromide (61 □L, 0.50 mmol). The reaction mixture was stirred at –78 °C for 3 h.

Purification with flash column chromatography on silica gel (1:6 Hexanes/EtOAc) provided 23.7 mg (74%) of (*3R*)-**5** as a colorless oil.
^{1}H NMR ($CDCl_3$) indicated a 55:45 mixture of the axial-Me and equatorial-Me conformers: □ 7.60-7.15 (m, 12H), 6.94-6.86 (m, 1H), 4.62-4.52 (two overlapping septets, 1H), 3.74 (d, *J* = 13.5 Hz, 1H □ 0.55 ax-Me), 3.22 (d, *J* = 13.5 Hz, 1H □ 0.55 ax-Me), 2.54 (d, *J* = 13.9 Hz, 1H □ 0.45 eq-Me), 2.39 (d, *J* = 13.8 Hz, 1H □ 0.45 eq-Me), 1.71 (s, 3H □ 0.45 eq-Me), 1.54 (two overlapping doublets, *J* = 6.9 Hz, 6H □ 0.45 eq-Me), 1.33 (d, *J* = 7.1 Hz, 3H □ 0.55 ax-Me), 1.29 (d, *J* = 7.1 Hz, 0.55 ax-Me), 0.72 (s, 3H □ 0.55 ax-Me).
^{1}H-^{1}H COSY ($CDCl_3$): Among other correlations, spin-coupling between the following benzylic protons is evident: □ 3.74 and 3.22; □ 2.54 and 2.39.
^{1}H-^{1}H EXSY ($CDCl_3$): EXSY confirms that the two species present in solution interconvert, consistent with our assignment as (*M*)- and (*P*)-conformers. Chemical exchange between the following equatorial and axial diastereotopic benzylic protons is evident: □ 3.74 and 2.39; □ 3.22 and 2.54. Chemical exchange between the accidentally equivalent isopropyl methyls (2) at □ 1.54 with the diastereotopic methyls at □ 1.33 and 1.29 is seen. Finally, chemical exchange between the equatorial Me at □ 1.71 and the axial Me at 0.72 is also evident. See end of experimental section of the Supporting Information for determination of exchange rate.
^{13}C NMR ($CDCl_3$) was consistent with an approximate 1:1 mixture of axial-Me and equatorial-Me conformers (44 resonances found for a possible 2 x 22 unique carbons): □ 173.4, 172.1, 165.3, 164.9, 140.64, 140.58, 139.77, 139.7, 138.6, 137.0, 134.2, 133.9, 132.3, 131.1, 130.8, 130.43, 130.40, 129.9, 129.77, 129.71, 129.47, 129.45, 129.39, 129.2, 128.5, 128.4, 128.2, 127.5, 126.7, 126.2, 124.7, 124.6, 68.5, 66.3, 53.6, 53.3, 47.6, 37.7, 28.5, 22.3, 22.0, 20.8, 20.6, 17.6.
HRMS calcd. for $C_{26}H_{26}ClN_2O$ (M+1) 417.1734, found 417.1743 (+2.2 ppm, +0.9 mmu).
$[\alpha]^{24}_D$= +31.4° (c = 0.15, $CHCl_3$). Chiral stationary phase HPLC (Chiralcel AD-H) indicated 97 %ee. Conversion to the corresponding quaternary amino acid confirmed (*R*)-stereochemistry (see below).

(*3S*)-5 from Phe-derived benzodiazepine (*3S*)-3c
The general procedure was followed with (*3S*)-**3c** (50 mg, 0.124 mmol), HMPA (130 μL, 0.745 mmol), LDA (99 μL, 0.149 mmol, 1.5M in hexanes), *n*-BuLi (60 μL, 0.149 mmol, 2.5M in hexanes) and methyl iodide (77 μL, 1.24 mmol). The reaction mixture was stirred at –78 °C for 2.5 hours. Purification with flash column chromatography on silica gel (1:6 EtOAc:hexanes) provided 32.9 mg (64%) of (*3S*)-**5** as a pale yellow oil.
Chiral stationary phase HPLC (Chiralcel AD-H) indicated 96 %ee and (*3S*)-stereochemistry (comparison with (*3R*)-**5** synthesized from (*3S*)-**2c** above).

(*3R*)-6
The general procedure was followed with (*3S*)-**2c** (50.0 mg, 0.15mmol), HMPA (160 □L, 0.90 mmol), LDA (123 □L, 0.18 mmol, 1.5M in hexanes), *n*-BuLi (74 □L, 0.18 mmol) and 4-methylbenzyl bromide (284.5 mg, 1.5 mmol). The reaction mixture was stirred at –78 °C for 6 h. Purification with flash column chromatography on silica gel (1:8 Hexanes/EtOAc) provided 45.0 mg (68%) of (*3R*)-**6** as a colorless oil,
^{1}H NMR ($CDCl_3$) indicated a 53:47 ratio of axial-Me and equatorial-Me conformers: □ 7.58 (t, J = 7.1 Hz, 2H), 7.50- 7.06 (unassigned aromatic protons, 8H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J*= 8.0 Hz, 1H), 4.60-4.53 (two overlapping septets, 1H), 3.70 (d, *J* = 13.6 Hz, 1H □ 0.53 ax-Me), 3.17 (d, *J* = 13.5 Hz, 1H □ 0.53 ax-Me), 2.49 (d, *J* = 13.7 Hz, 1H □ 0.47 eq-Me), 2.35 (s, 3H □ 0.53 ax-Me),

2.33 (d, *J* = 13.7 Hz, 1H □ 0.47 eq-Me), 2.28 (s, 3H □ 0.47 eq-Me), 1.70 (s, 3H □ 0.47 eq-Me), 1.56-1.52 (m, 6H x 0.53 ax-Me), 1.327 (d, *J* = 6.8 Hz, 3H x 0.47 eq-Me), 1.289 (d, *J* = 6.8 Hz, 3H x 0.47 eq-Me), 0.71 (s, 3H □ 0.52 ax-Me).
^{13}C NMR ($CDCl_3$) was consistent with an approximate 1:1 mixture of conformers (44 resonances found for a possible 2 x 23 unique carbons): □ 173.4, 172.3, 165.2, 164.8, 140.7, 140.6, 139.8, 139.7, 136.2, 135.7, 135.4, 134.3, 133.9, 133.8, 132.1, 131.0, 130.8, 130.4, 129.9, 129.7, 129.6, 129.5, 129.4, 129.2, 128.9, 128.5, 128.4, 128.3, 124.7, 124.6, 68.6, 66.3, 53.6, 53.2, 47.1, 37.3, 28.4, 22.3, 22.0, 21.2, 21.1, 20.7, 20.6, 17.6.
HRMS calcd. for $C_{27}H_{28}ClN_2O$ (M+1) 431.1890, found 431.1892 (+0.4 ppm, +0.2 mmu).
$[\square]^{21}_D$= +31.2° (c= 0.16, $CHCl_3$). Chiral stationary phase HPLC (Chiralcel AD-H) indicated 95 %ee. Stereochemistry assigned as (*R*)- based on the sign of rotation of the corresponding quaternary amino acid (see below).

(*3R*)-7
The general procedure was followed with (*3S*)-**2c** (50.0 mg, 0.15mmol), HMPA (160 □L, 0.90 mmol), LDA (123 □L, 0.18 mmol), *n*-BuLi (74 □L, 0.18 mmol) and 2-phenylbenzyl bromide (284.5 mg, 1.5 mmol). The reaction mixture was stirred at –78 °C for 10 h. Purification with flash column chromatography on silica gel (1:8 Hexanes/EtOAc) provided 53.0 mg (70%) of (*3R*)-**7** as a colorless oil.
^{1}H NMR ($CDCl_3$) indicated a 50:50 mixture of axial-Me and equatorial-Me conformers: □ 8.11 (dd, *J* = 7.8, 1.2 Hz, 1H x 0.5), 7.58-6.99 (unassigned protons, 16.5 H), 4.56 (septet, *J* = 7.1 Hz, 1H □ 0.50), 4.49 (septet, *J* = 6.9 Hz, 1H □ 0.50), 3.68 (d, *J* = 13.5 Hz, 1H x 0.5 ax-Me), 3.63 (d, *J* = 13.5 Hz, 1H x 0.5 ax-Me) 2.51 (apparent s, actually collapsed AB pattern of benzylic protons of eq-Me conformer, 2H x 0.5), 1.54 (d, *J* = 6.9 Hz, 3H □ 0.5), 1.46 (d, *J* = 6.7 Hz, 3H □ 0.5), 1.40 (s, 3H □ 0.5 eq-Me), 1.29 (d, *J* = 7.1 Hz, 3H □ 0.5), 1.21 (d, *J* = 7.1 Hz, 3H □ 0.5), 0.33 (s, 3H □ 0.50 ax-Me).
^{13}C NMR ($CDCl_3$) was consistent with a 1:1 mixture of conformers (55 resonances found for a possible 2 x 28 unique carbons): □ 172.8, 172.1, 165.0, 164.5, 144.1, 143.2, 142.8, 141.7, 140.6, 140.5, 139.9, 139.5, 135.9, 134.7, 134.0, 133.9, 133.6, 131.0, 130.7, 130.6, 130.4, 130.3, 130.1, 129.9, 129.8, 129.7, 129.5, 129.4, 129.3, 129.2, 129.1, 128.4, 128.21, 128.19, 128.16, 127.2, 126.9, 126.5, 126.37, 126.30, 126.2, 124.7, 124.6, 69.0, 67.3, 53.5, 53.2, 42.4, 33.6, 28.0, 22.2, 22.0, 20.8, 20.5, 17.2.
HRMS calcd. for $C_{32}H_{30}ClN_2O$ (M+1) 493.2047, found 493.2051 (+0.9 ppm, +0.4 mmu).
$[\square]^{24}_D$= +163.7° (c = 0.14, $CHCl_3$). Chiral stationary phase HPLC (AD-H) indicated 99% ee. The stereochemistry is assumed to be (*R*) based on other retentive alkylations.

(*3R*)-8
The general procedure was followed with (*3S*)-**2c** (145.8 mg, 0.45mmol), HMPA (481 □l, 2.69 mmol), LDA (370 □L, 0.54 mmol, 1.5M in hexanes), *n*-BuLi (221 □L, 0.54 mmol, 2.5M in hexanes) and allyl bromide (350 □L, 4.5 mmol). The reaction mixture was stirred at –78 °C for 4 h. Purification with flash column chromatography on silica gel (1:10 Hexanes/EtOAc) provided 124.7 mg (76%) of (*3R*)-**8** as a colorless oil,
^{1}H NMR ($CDCl_3$) indicated a 50:50 mixture of axial-Me and equatorial-Me conformers: □ 7.62-7.55 (m, 2H), 7.48-7.37 (m, 4H), 7.31 (dd, *J* = 8.7, 5.5 Hz, 1H), 7.19 (dd, *J* = 7.6 Hz, 2.6 Hz, 1H), 6.29-6.20 (m, 1H □ 0.5), 5.61-5.52 (m, 1H □ 0.5), 5.22 (apparent d, *J* = 16.3 Hz, 1H □ 0.5), 5.17 (apparent d, *J* = 10.3 Hz, 1H x 0.5), 4.94 (apparent d, *J* = 10.3 Hz , 1H □ 0.5), 4.63 (apparent d, *J* =

16.3 Hz , 1H □ 0.5), 4.56-4.45 (two overlapping septets, 1H), 3.101 (dd, *J* = 13.9, 5.7 Hz, 1H □ 0.5 ax-Me), 2.737 (dd, *J* = 13.9, 8.3 Hz, 1H □ 0.5 ax-Me), 1.93-1.83 (m, 2H x 0.5), 1.83 (s, 3H □ 0.5 eq-Me), 1.510 (d, *J* = 3.5Hz, 3H x 0.5), 1.497 (d, *J* = 3.5 Hz, 3H x 0.5), 1.287 (d, *J* = 7.1 Hz, 3H x 0.5), 1.267 (d, *J* = 7.1 Hz, 3H x 0.5), 0.78 (s, 3H □ 0.5 ax-Me).
^{13}C NMR ($CDCl_3$) was consistent with a 50:50 mixture of conformers (40 resonances found from 2 x 20 unique carbons): □ 173.1, 172.3, 165.2, 165.0, 140.6, 140.3, 139.6, 139.5, 135.8, 134.1, 133.9, 134.1, 133.9, 132.9, 130.9, 130.8, 130.5, 130.4, 129.8, 129.7, 129.4, 129.34, 129.30, 128.5, 124.8, 124.7, 118.3, 118.0, 67.5, 65.8, 53.4, 53.1, 47.3, 37.2, 28.6, 22.2, 22.1, 20.7, 20.6, 18.0.
HRMS calcd. for $C_{22}H_{24}ClN_2O$ (M+1) 367.1577, found 367.1577.
$[\square]^{24}_D$= + 50.0 (c = 0.33 , $CHCl_3$). Chiral stationary phase HPLC (Chiralcel OD) indicated 94 %ee. The stereochemistry is assumed to be (*R*) based on other retentive alkylations.

(*3S*)-10 from (*3S*)-3c
The general procedure was followed with (*3S*)-**3c** (20 mg, 0.0496 mmol), HMPA (52 μL, 0.298 mmol), LDA (40 μL, 0.0595 mmol, 1.5M in hexanes), n-BuLi (24 μL, 0.0595 mmol, 2.5M in hexanes) and allyl bromide (43 μL, 0.496 mmol). The reaction mixture was stirred at –78 °C for 20 minutes. Purification with flash column chromatography on silica gel (1 EtOAc: 8 Hex) provided 12.1 mg (57%) of (*3S*)-**5** as a pale yellow oil.
^{1}H NMR ($CDCl_3$) indicated a 60:40 mixture of conformers: □ 7.6-6.96 (several multiplets, 13H), 6.41-6.32 (m, 1H x 0.4), 5.71-5.62 (m, 1H x 0.6), 5.27 (apparent d, *J* = 10.0 Hz, 1H x 0.4), 5.23 (apparent d, *J* = 16.3 Hz, 1H x 0.4), 5.01 (dd, *J* = 10.0, 1.6 Hz, 1H x 0.6), 4.65 (dd, *J* = 16.8, 1.6 Hz, 1H x 0.6), 4.56 (two overlapped septets, *J* = 6.9 Hz, 1H), 3.67 (d, *J* = 14.6 Hz, 1H x 0.6), 3.39 (d, *J* = 14.6 Hz, 1H x 0.6), 3.03 (complex d, *J* = 14.7 Hz, 1H x 0.4), 2.69 (dd, *J* = 14.7, 8.7 Hz, 1H x 0.4), 2.46 (d, *J* = 14.3 Hz, 1H x 0.4), 2.42 (d, *J* = 14.3 Hz, 1H x 0.4), 1.88 (dd, *J* = 15.0, 6.8 Hz, 1H x 0.6), 1.59-1.54 (m, 1H x 0.6), 1.52 (two overlapped doublets, *J* = 6.9 Hz, 6H x 0.4), 1.30 (d, *J* = 7.0 Hz, 3H x 0.6), 1.285 (d, *J* = 7.0 Hz, 3H x 0.6).
^{13}C NMR ($CDCl_3$) was consistent with a near 1:1 mixture of conformers (48 resonances found for 2 x 24 unique carbons): □ 171.9, 171.6, 165.0, 164.7, 140.4, 140.0, 139.8, 139.6, 138.5, 136.6, 135.9, 134.1, 133.6, 132.9, 132.3, 130.9, 130.50, 130.48, 130.4, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 129.2, 128.43, 128.36, 128.2, 127.5, 126.6, 126.3, 124.74, 124.70, 118.4, 118.2, 70.4, 70.0, 53.4, 53.3, 43.2, 42.6, 34.5, 32.5, 22.1, 21.9, 20.5, 20.4.
HRMS: calcd for $C_{28}H_{27}N_2OCl$ 443.1890, found 443.1898 (+1.7 ppm, +0.8 mmu).
$[\square]^{21}_D$= +72.1° (c = 0.315, $CHCl_3$). Chiral stationary phase HPLC (Chiralcel AD-H) indicated 86 %ee. The stereochemistry is assumed to be (*S*) on the basis of other retentive alkylations.

(*3S*)-9: deuteration of enolate derived from (*3S*)-2c
A solution of (*3S*)-**2c** (16.6 mg, 0.05 mmol) and HMPA (53 □l, 0.3 mmol) in anhydrous THF (1.0 mL) was cooled to –78 °C under nitrogen in a dry ice-acetone bath and LDA (41.0 □l , 0.06 mmol, 1.5M in hexanes) was added dropwise via syringe at –78 °C. After the mixture was stirred for 30 min, *n*-BuLi (25 □l, 0.06 mmol, 2.5M in hexanes) was added and then the reaction mixture was stirred for 20 min. The enolate was quenched at –78 °C with a mixture of deuteriotrifluoroacetic acid and deuterium oxide (4 μL of D-OTFA in 200.0 μL of D_2O). Workup and purification with flash column chromatography on silica gel (1:5 Hexanes/EtOAc) provided 14.2 mg (85%) of (*3S*)-**9** as a pale yellow oil (96%D by ^{1}H NMR).
^{1}H NMR ($CDCl_3$) □ 7.62-7.58 (m, 2H), 7.50-7.33 (m, 5H), 7.28-7.25 (m, 1H), 4.56 (septet, *J* = 6.8 Hz), 1.69 (s, 3H), 1.48 (d, *J* = 6.9 Hz, 3H), 1.20 (d, *J* = 7.1 Hz).

^{13}C NMR ($CDCl_3$) □170.8, 166.7, 140.4, 138.1, 133.0, 130.64, 130.59, 130.3, 129.4, 129.3, 128.6, 125.3, 59.7 (t, $^1J_{CD}$ = 19.6 Hz), 20.7, 17.1.
FABMS *m/z* 328.1 (M+1),
$[\square]^{24}_D$= +219.2° (c = 0.37, $CHCl_3$). Chiral stationary phase HPLC (Chiralcel AD) indicated 99%ee and (*3S*)-stereochemistry

General procedure for hydrolysis of *N-i*-Pr-1,4-benzodiazepine2-ones to the corresponding quaternary amino acids.
The benzodiazepine to be hydrolyzed (0.1 mmol) was combined with hydrochloric acid (9.0M, 2.0mL) in a pressure tube (Teflon screw cap) and heated at 140 °C (bath temperature) for 3 days. Water (2.0 mL) was added and then the mixture was extracted with EtOAc (3 x 3mL). The water layer was separated, concentrated in vacuo and the residue was dissolved in EtOH (2.0 mL). Propylene oxide (0.3 mL) was added, and the resulting solution was heated at reflux for 30 minutes. Upon cooling the precipitated solid was collected and washed with ethyl acetate and acetone, affording the corresponding free amino acid.

(*R*)-□-methylphenylalanine 11
41.6 mg (0.1 mmol) of (*3R*)-**5** was treated as above to afford 9.0 mg of (*R*)-□-methylphenylalanine **11** (50%).
^{1}H NMR (d_6-DMSO) □7.60-7.15 (br m, 7H), 2.79 (d, *J* = 13.7 Hz, 1H), 2.51 (d, *J* = 13.7 Hz, 1H), 1.23 (s, 3H). This spectrum was identical in every aspect to commercial □-methylphenylalanine.
$[\square]^{26}_D$= + 25.6 (c= 1.25, H_2O). Acros (*S*)-□-methylphenylalanine (item# 27543-2500) is levorotatory: $[\square]^{25}_D$= -24.8°, (c = 1.25, H_2O). We thus assign (*R*)-stereochemistry to our synthesized amino acid.

(*R*)-□-methyl-(4-methylphenyl)alanine 12
33.1 mg (0.77 mmol) of (*3R*)-**6** was treated as above to afford 9.2 mg of □-methyl-(4-methylphenyl)alanine **12** (62%).
^{1}H NMR (d_6-DMSO) □7.50-6.80 (br m, 6H), 2.96 (d, *J* = 13.5 Hz, 1H), 2.73 (d, *J* = 13.5 Hz, 1H), 2.26 (s, 3H), 1.22 (s, 3H).
HRMS: calcd for $C_{11}H_{15}NO_2$ 194.1181, found 194.1185 (+2.0 ppm, +0.4 mmu).
$[\square]^{19}_D$= +16.6° (c= 0.10, H_2O).
The optical rotations of the enantiomers of this compound are not known in the literature—we assigned the (*R*)-configuration based on the positive sign of the optical rotation, and the structural similarity with □-methylphenylalanine **11**.

Dynamic NMR Studies of 1b,1c, and 5
NMR probe temperatures were determined by calibration with ethylene glycol. The barriers to inversion of **1b** and **1c** were determined by achieving coalescence in d_6-DMSO on a 400 MHz spectrometer. **1b** : T_c(methylene protons) = 117 °C, Δ□ = 316.4 Hz, *J* = 10.8 Hz, $\Delta G^{\ddagger}$ = 18.0 kcal/mol (lit.[5] 17.6 kcal/mol in d_5-pyridine). **1c**: T_c(*i*-Pr methyl protons) = 159 °C, Δ□ = 89.4 Hz, $\Delta G^{\ddagger}$ = 21.1 kcal/mol. The barrier to inversion in **5** in CDCl3 at 24 °C was determined by EXSY[6] (400 MHz), using a mixing time of 1 sec and a relaxation delay of 2 sec. Since the M and P conformers exist in a nearly 1:1 ratio, we made the simplifying assumption that the M->P and P->M exchange rates are equal.

B. Tabulation of HPLC Conditions and Retention Times

Reported retention times are determined from racemic and enantiomerically enriched/pure samples. The HPLC columns are not thermostatted and as a consequence retention times are subject to day to day variability (cf. cpds **2c**, **9**; **9** is the deuterated analogue of **2c**).

compound	column	solvent, flow rate	fast enantiomer (config) retention time	slow enantiomer (config) retention time
2a	AD	10% isopropanol-hexane 1 mL/min	11.0 min (*3R*)	13.9 min (*3S*)
3a	OD	3% isopropanol-hexane 1 mL/min	27.4 min (*3R*)	30.9 min (*3S*)
2b	AD	5% isopropanol-hexane 1 mL/min	14.7 min (*3R*)	16.5 min (*3S*)
2c	AD	1% isopropanol-hexane 1 mL/min	16.4 min (*3R*)	18.2 min (*3S*)
3c	AD	5% isopropanol-hexane 1 mL/min	14.7 min (*3R*)	16.2 min (*3S*)
4	AD-H	2% isopropanol-hexane 1 mL/min	19.4 min	24.4
5	AD-H	1% isopropanol-hexane 1 mL/min	20.2 min (*3S*)	22.6 min (*3R*)
6	AD-H	1% isopropanol-hexane 1 mL/min	12.8 min (*3R*)	18.2 min (*3S*)
7	AD-H	1% isopropanol-hexane 1 mL/min	13.6 min major enantiomer from (*3S*)-**2c**	16.4 min
8	OD	100% hexane 1 mL/min	17.9 min	19.1 min major enantiomer from (*3S*)-**2c**
9	AD	1% isopropanol-hexane 1 mL/min	15.8 min (*3R*)	16.9 min (*3S*)
10	AD-H	1% isopropanol-hexane 1 mL/min	13.3 min	14.3 min major enantiomer from (*3S*)-**3c**

C. Computational Details, Absolute Energies, and Cartesian Coordinates for Calculated Structures

B3LYP/6-31G* equilibrium geometries and ring inversion transition structures of the enolates, and single point electronic energies ($\square_0$) at the B3LYP/6-31+G*//B3LYP/6-31G* level were obtained using Gaussian 98 (v.A.11). Vibrational frequency analysis was used to identify stationary points as minima (no imaginary frequencies) or transition states (1 imaginary frequency). Displacement vectors associated with the sole imaginary frequencies confirmed that the located transition structures were associated with the ring inversion process. The standard Gaussian 98 statistical mechanics calculations were used to determine the enthalpic corrections (H_{corr}) and total entropy (S_{tot}) from the B3LYP/6-31G* vibrational frequencies and temperature (195 K). The free energy correction (G_{corr}) was obtained from $G_{corr} = H_{corr} - TS_{tot}$; relative free energies ΔG_{195} were obtained by comparing values of ($\square_0 + G_{corr}$)

	R_2	structure	$\square_0$ (hartrees)	H_{corr}(195 K) (kcal/mol)	S_{tot}(195 K) (cal/molK)	G_{corr}(195 K) (kcal/mol)	ΔG_{195} (kcal/mol)
13b	Me	equil. geometry	-841.643735	176.99	106.25	156.3	0
		ring inv. transition structure	-841.624731	176.63	101.80	156.8	12.4
13c	*i*-Pr	equil. geometry	-920.270594	212.51	114.84	190.1	0
		ring inv. transition structure	-920.243390	212.30	111.76	190.5	17.5

Coordinates for 13b (B3LYP/6-31G* equilibrium geometry)

```
HEADER
REMARK 13b B3LYP/6-31G* equilibrium geometry
HETATM    1  C           1       0.000   0.000   0.000
HETATM    2  C           1       0.000   0.000   1.417
HETATM    3  C           1       1.212   0.000  -0.707
HETATM    4  N           1      -1.249  -0.074  -0.695
HETATM    5  C           1       2.440  -0.045  -0.045
HETATM    6  C           1       1.260  -0.015   2.058
HETATM    7  H           1       1.191   0.006  -1.792
HETATM    8  C           1      -1.246  -0.724  -1.997
HETATM    9  C           1      -1.243   0.175   2.192
HETATM   10  C           1      -2.084   1.095  -0.638
HETATM   11  C           1       2.458  -0.052   1.351
HETATM   12  H           1       3.365  -0.075  -0.616
HETATM   13  H           1       1.284   0.008   3.143
HETATM   14  H           1      -0.799  -0.119  -2.801
HETATM   15  N           1      -2.194   1.039   1.838
HETATM   16  C           1      -1.389  -0.417   3.532
HETATM   17  C           1      -2.439   1.611   0.665
HETATM   18  O           1      -2.587   1.519  -1.693
HETATM   19  H           1      -2.279  -0.925  -2.289
HETATM   20  H           1      -0.698  -1.668  -1.913
HETATM   21  H           1       3.404  -0.074   1.890
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HETATM   22  C           1      -2.313   0.117   4.467
HETATM   23  C           1      -0.690  -1.579   3.940
HETATM   24  C           1      -3.447   2.743   0.648
HETATM   25  C           1      -0.878  -2.146   5.200
HETATM   26  C           1      -2.495  -0.449   5.722
HETATM   27  H           1      -2.882   0.989   4.163
HETATM   28  H           1      -0.001  -2.052   3.247
HETATM   29  H           1      -3.027   3.661   0.211
HETATM   30  H           1      -3.756   2.959   1.676
HETATM   31  H           1      -4.337   2.503   0.048
HETATM   32  C           1      -1.777  -1.588   6.112
HETATM   33  H           1      -0.320  -3.043   5.466
HETATM   34  H           1      -3.207   0.004   6.411
HETATM   35  H           1      -1.924  -2.032   7.094
CONECT    1    2    3    4
CONECT    2    1    6    9
CONECT    3    1    5    7
CONECT    4    1    8   10
CONECT    5    3   11   12
CONECT    6    2   11   13
CONECT    7    3
CONECT    8    4   14   19   20
CONECT    9    2   15   16
CONECT   10    4   17   18
CONECT   11    5    6   21
CONECT   12    5
CONECT   13    6
CONECT   14    8
CONECT   15    9   17
CONECT   16    9   22   23
CONECT   17   10   15   24
CONECT   18   10
CONECT   19    8
CONECT   20    8
CONECT   21   11
CONECT   22   16   26   27
CONECT   23   16   25   28
CONECT   24   17   29   30   31
CONECT   25   23   32   33
CONECT   26   22   32   34
CONECT   27   22
CONECT   28   23
CONECT   29   24
CONECT   30   24
CONECT   31   24
CONECT   32   25   26   35
CONECT   33   25
CONECT   34   26
CONECT   35   32
END
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Coordinates for 13b (B3LYP/6-31G* ring inversion transition structure)

```
HEADER
REMARK 13b B3LYP/6-31G*
REMARK ring inversion transition structure
HETATM    1  C           1       0.000   0.000   0.000
HETATM    2  C           1       0.000   0.000   1.442
HETATM    3  C           1       1.249   0.000  -0.650
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HETATM    4  N           1      -1.148  -0.071  -0.845
HETATM    5  C           1       2.470  -0.179   0.014
HETATM    6  C           1       1.238  -0.296   2.056
HETATM    7  H           1       1.286   0.127  -1.723
HETATM    8  C           1      -1.162   0.267   2.310
HETATM    9  C           1      -0.907  -0.434  -2.238
HETATM   10  C           1      -2.534   0.166  -0.553
HETATM   11  C           1       2.456  -0.386   1.383
HETATM   12  H           1       3.396  -0.186  -0.558
HETATM   13  H           1       1.236  -0.444   3.129
HETATM   14  N           1      -2.431   0.339   1.945
HETATM   15  H           1      -1.866  -0.681  -2.685
HETATM   16  C           1      -0.984   0.568   3.759
HETATM   17  C           1      -3.059   0.315   0.784
HETATM   18  O           1      -3.313   0.205  -1.523
HETATM   19  H           1      -0.466   0.388  -2.824
HETATM   20  H           1      -0.225  -1.291  -2.288
HETATM   21  H           1       3.368  -0.602   1.936
HETATM   22  C           1      -1.967   0.142   4.684
HETATM   23  C           1       0.064   1.359   4.288
HETATM   24  C           1      -4.565   0.508   0.832
HETATM   25  C           1       0.130   1.684   5.642
HETATM   26  C           1      -1.898   0.462   6.035
HETATM   27  H           1      -2.799  -0.439   4.300
HETATM   28  H           1       0.826   1.746   3.618
HETATM   29  H           1      -5.114  -0.341   0.399
HETATM   30  H           1      -4.894   1.394   0.269
HETATM   31  H           1      -4.864   0.625   1.878
HETATM   32  C           1      -0.844   1.235   6.536
HETATM   33  H           1       0.949   2.309   5.998
HETATM   34  H           1      -2.674   0.101   6.709
HETATM   35  H           1      -0.787   1.483   7.594
CONECT    1    2    3    4
CONECT    2    1    6    8
CONECT    3    1    5    7
CONECT    4    1    9   10
CONECT    5    3   11   12
CONECT    6    2   11   13
CONECT    7    3
CONECT    8    2   14   16
CONECT    9    4   15   19   20
CONECT   10    4   17   18
CONECT   11    5    6   21
CONECT   12    5
CONECT   13    6
CONECT   14    8   17
CONECT   15    9
CONECT   16    8   22   23
CONECT   17   10   14   24
CONECT   18   10
CONECT   19    9
CONECT   20    9
CONECT   21   11
CONECT   22   16   26   27
CONECT   23   16   25   28
CONECT   24   17   29   30   31
CONECT   25   23   32   33
CONECT   26   22   32   34
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CONECT   27   22
CONECT   28   23
CONECT   29   24
CONECT   30   24
CONECT   31   24
CONECT   32   25   26   35
CONECT   33   25
CONECT   34   26
CONECT   35   32
END
```

Coordinates for 13c (B3LYP/6-31G* equilibrium geometry)

```
HEADER
REMARK 13c B3LYP/6-31G* equilibrium geometry
HETATM    1  C           1       0.000   0.000   0.000
HETATM    2  C           1       0.000   0.000   1.414
HETATM    3  C           1       1.210   0.000  -0.712
HETATM    4  N           1      -1.273  -0.022  -0.664
HETATM    5  C           1       2.431  -0.106  -0.050
HETATM    6  C           1       1.255  -0.097   2.061
HETATM    7  H           1       1.182   0.045  -1.798
HETATM    8  C           1      -1.431  -0.837  -1.880
HETATM    9  C           1      -1.233   0.314   2.154
HETATM   10  C           1      -1.824   1.314  -0.705
HETATM   11  C           1       2.447  -0.166   1.349
HETATM   12  H           1       3.359  -0.142  -0.617
HETATM   13  H           1       1.281  -0.092   3.147
HETATM   14  H           1      -0.922  -0.369  -2.742
HETATM   15  N           1      -2.056   1.290   1.766
HETATM   16  C           1      -1.479  -0.242   3.495
HETATM   17  C           1      -2.162   1.883   0.580
HETATM   18  O           1      -2.104   1.854  -1.790
HETATM   19  C           1      -2.922  -0.953  -2.235
HETATM   20  C           1      -0.863  -2.247  -1.664
HETATM   21  H           1       3.392  -0.242   1.884
HETATM   22  C           1      -2.372   0.390   4.395
HETATM   23  C           1      -0.901  -1.458   3.932
HETATM   24  H           1      -3.471  -1.408  -1.401
HETATM   25  H           1      -3.046  -1.591  -3.120
HETATM   26  H           1      -3.345   0.029  -2.446
HETATM   27  H           1      -1.356  -2.722  -0.807
HETATM   28  H           1       0.213  -2.249  -1.474
HETATM   29  H           1      -1.053  -2.860  -2.554
HETATM   30  C           1      -2.938   3.183   0.527
HETATM   31  C           1      -1.171  -1.986   5.194
HETATM   32  C           1      -2.637  -0.139   5.652
HETATM   33  H           1      -2.846   1.308   4.065
HETATM   34  H           1      -0.244  -2.001   3.260
HETATM   35  H           1      -2.305   4.026   0.209
HETATM   36  H           1      -3.330   3.406   1.524
HETATM   37  H           1      -3.769   3.141  -0.191
HETATM   38  C           1      -2.038  -1.334   6.073
HETATM   39  H           1      -0.706  -2.927   5.487
HETATM   40  H           1      -3.322   0.386   6.317
HETATM   41  H           1      -2.251  -1.748   7.056
CONECT    1    2    3    4
CONECT    2    1    6    9
CONECT    3    1    5    7
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CONECT    4    1    8   10
CONECT    5    3   11   12
CONECT    6    2   11   13
CONECT    7    3
CONECT    8    4   14   19   20
CONECT    9    2   15   16
CONECT   10    4   17   18
CONECT   11    5    6   21
CONECT   12    5
CONECT   13    6
CONECT   14    8
CONECT   15    9   17
CONECT   16    9   22   23
CONECT   17   10   15   30
CONECT   18   10
CONECT   19    8   24   25   26
CONECT   20    8   27   28   29
CONECT   21   11
CONECT   22   16   32   33
CONECT   23   16   31   34
CONECT   24   19
CONECT   25   19
CONECT   26   19
CONECT   27   20
CONECT   28   20
CONECT   29   20
CONECT   30   17   35   36   37
CONECT   31   23   38   39
CONECT   32   22   38   40
CONECT   33   22
CONECT   34   23
CONECT   35   30
CONECT   36   30
CONECT   37   30
CONECT   38   31   32   41
CONECT   39   31
CONECT   40   32
CONECT   41   38
END
```

Coordinates for 13c (B3LYP/6-31G* ring inversion transition structure)

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HEADER
REMARK 13c B3LYP/6-31G*
REMARK ring inversion transition structure
HETATM    1  C           1       0.000   0.000   0.000
HETATM    2  C           1       0.000   0.000   2.860
HETATM    3  C           1       1.254   0.000   0.713
HETATM    4  C           1      -1.154  -0.229   0.774
HETATM    5  C           1      -1.178  -0.236   2.172
HETATM    6  C           1       1.175   0.107   2.120
HETATM    7  H           1      -2.095  -0.388   0.275
HETATM    8  H           1      -2.122  -0.400   2.689
HETATM    9  H           1       2.108   0.248   2.654
HETATM   10  H           1       0.026   0.074   3.945
HETATM   11  N           1      -0.192   0.233  -1.400
HETATM   12  C           1       2.608  -0.105   0.128
HETATM   13  N           1       2.947   0.150  -1.119
HETATM   14  C           1      -1.558   0.510  -1.924
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HETATM   15  H           1      -1.339   0.859  -2.931
HETATM   16  C           1       3.758  -0.569   0.949
HETATM   17  C           1       6.068  -1.518   2.345
HETATM   18  C           1       5.059  -0.083   0.669
HETATM   19  C           1       3.672  -1.564   1.952
HETATM   20  C           1       4.799  -2.027   2.630
HETATM   21  C           1       6.181  -0.541   1.349
HETATM   22  H           1       5.158   0.659  -0.117
HETATM   23  H           1       2.704  -1.995   2.189
HETATM   24  H           1       4.681  -2.804   3.385
HETATM   25  H           1       7.159  -0.126   1.104
HETATM   26  C           1       0.818   0.412  -2.427
HETATM   27  C           1       2.244   0.410  -2.209
HETATM   28  O           1       0.408   0.579  -3.593
HETATM   29  C           1      -2.419  -0.747  -2.160
HETATM   30  H           1      -2.745  -1.271  -1.257
HETATM   31  H           1      -1.849  -1.455  -2.771
HETATM   32  H           1      -3.321  -0.467  -2.722
HETATM   33  C           1      -2.291   1.688  -1.253
HETATM   34  H           1      -2.680   1.493  -0.251
HETATM   35  H           1      -3.138   1.977  -1.890
HETATM   36  H           1      -1.616   2.549  -1.184
HETATM   37  H           1       6.946  -1.875   2.880
HETATM   38  C           1       3.052   0.635  -3.476
HETATM   39  H           1       2.836   1.605  -3.947
HETATM   40  H           1       2.851  -0.123  -4.248
HETATM   41  H           1       4.115   0.598  -3.217
CONECT    1    3    4   11
CONECT    2    5    6   10
CONECT    3    1    6   12
CONECT    4    1    5    7
CONECT    5    2    4    8
CONECT    6    2    3    9
CONECT    7    4
CONECT    8    5
CONECT    9    6
CONECT   10    2
CONECT   11    1   14   26
CONECT   12    3   13   16
CONECT   13   12   27
CONECT   14   11   15   29   33
CONECT   15   14
CONECT   16   12   18   19
CONECT   17   20   21   37
CONECT   18   16   21   22
CONECT   19   16   20   23
CONECT   20   17   19   24
CONECT   21   17   18   25
CONECT   22   18
CONECT   23   19
CONECT   24   20
CONECT   25   21
CONECT   26   11   27   28
CONECT   27   13   26   38
CONECT   28   26
CONECT   29   14   30   31   32
CONECT   30   29
CONECT   31   29
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CONECT   32   29
CONECT   33   14   34   35   36
CONECT   34   33
CONECT   35   33
CONECT   36   33
CONECT   37   17
CONECT   38   27   39   40   41
CONECT   39   38
CONECT   40   38
CONECT   41   38
END
```
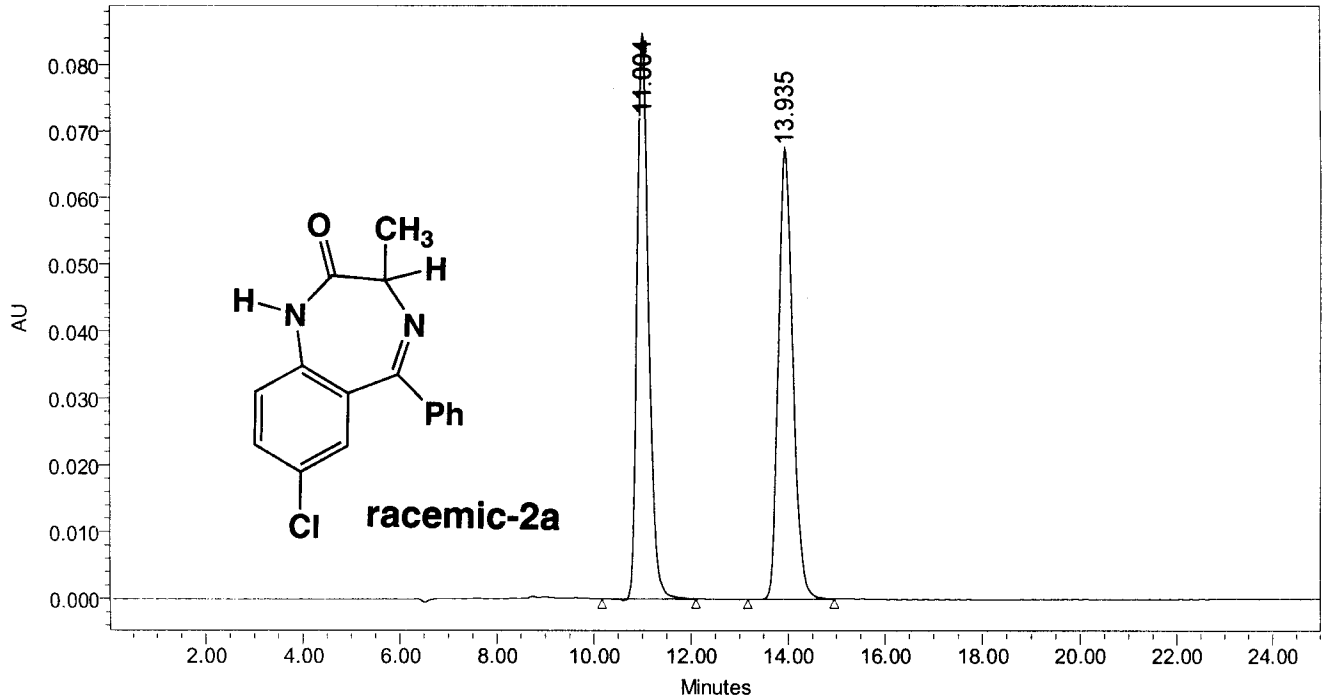

[1] Sternbach, L. H.; Fryer, R. I.; Metlesics, W.; Reeder, E.; Sach, G.; Saucy, G.; Stempel, A. *J. Org. Chem.* **1962**, *27*, 3788-3796.
[2] Hart, B. R.; Rush, D. J.; Shea, K. J. *J. Am. Chem. Soc.* **2000**, *122*, 460-465.
[3] Beard, C. D.; Baum, K.; Grakauskas, V. *J. Org. Chem.* **1973**, *38*, 3673-3677.
[4] Sunjic, V.; Kajfez, F.; Stromar, I.; Blazevic, N.; Kolbah, D. *J. Heterocyclic Chem.* **1973**, *10*, 591-599.
[5] Linscheid, P.; Lehn, J.-M. *Bull. Chim. Soc. Fr.* **1967**, 992-997.
[6] Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935-967.

S16

Project Name: HONGWU
Reported by User: JOE

SAMPLE INFORMATION

Sample Name:	HWZ-II-P137	Acquired By:	HongWu
Sample Type:	Unknown	Date Acquired:	3/5/03 1:14:04 PM
Vial:	1	Acq. Method:	10%B Isopropanol
Injection #:	1	Date Processed:	3/5/03 1:44:16 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	25.00 Minutes	Sample Set Name:	Hongwu

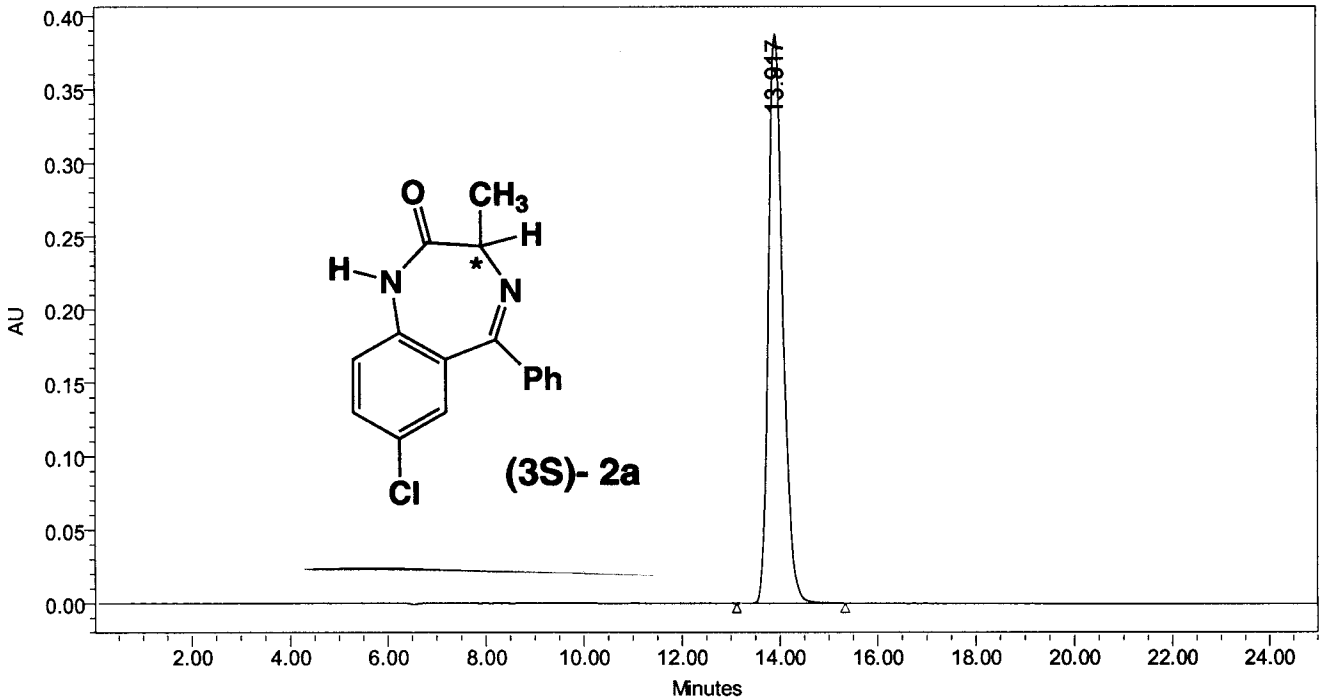


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.004	1399071	50.06	84693	55.67
2	13.935	1395552	49.94	67429	44.33

Project Name: HONGWU
Reported by User: JOE

SAMPLE INFORMATION

Sample Name:	HWZ-III-P15	Acquired By:	HongWu
Sample Type:	Unknown	Date Acquired:	3/5/03 2:04:42 PM
Vial:	1	Acq. Method:	10%B Isopropanol
Injection #:	1	Date Processed:	3/5/03 2:30:59 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	25.00 Minutes	Sample Set Name:	Hongwu

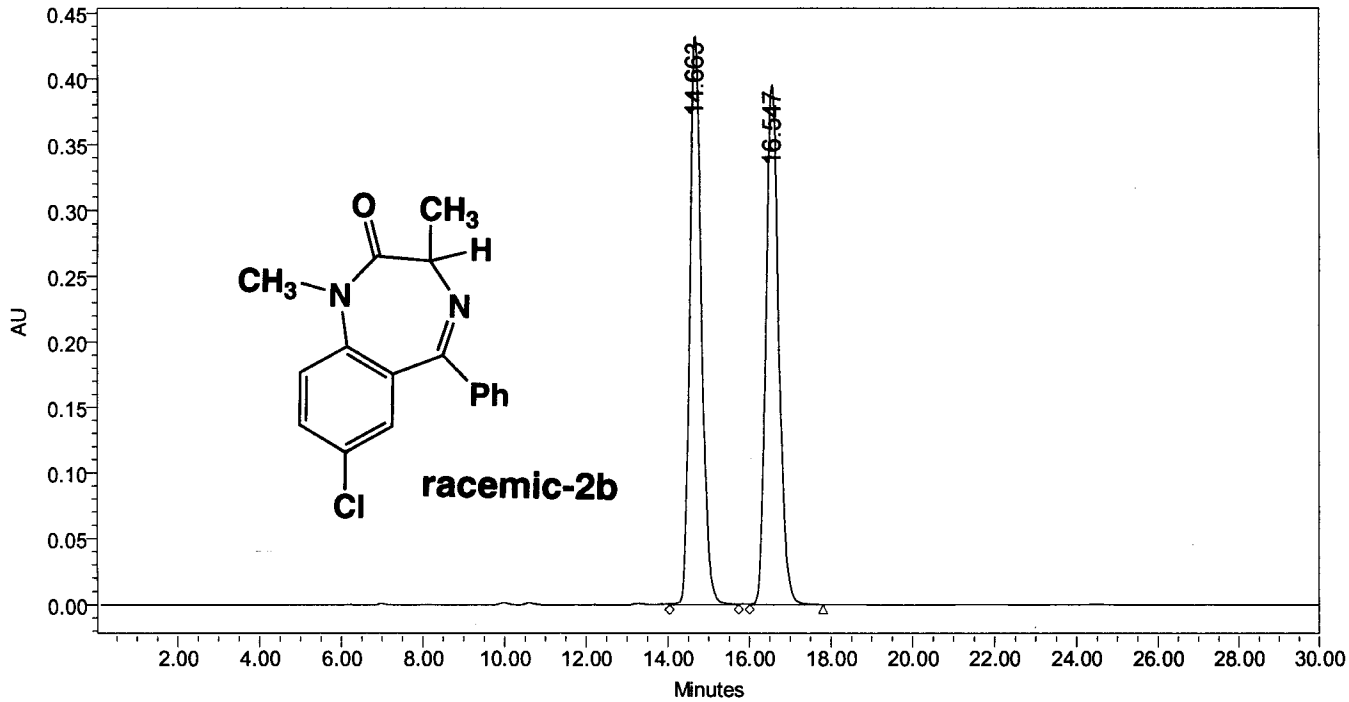


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.917	7930531	100.00	387021	100.00

Project Name: HONGWU
Reported by User: JOE

SAMPLE INFORMATION

Sample Name:	HWZ-II-P143	Acquired By:	HongWu
Sample Type:	Unknown	Date Acquired:	3/13/03 12:04:49 PM
Vial:	1	Acq. Method:	5%B Isopropanol
Injection #:	1	Date Processed:	3/13/03 2:00:01 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	30.00 Minutes	Sample Set Name:	Hongwu

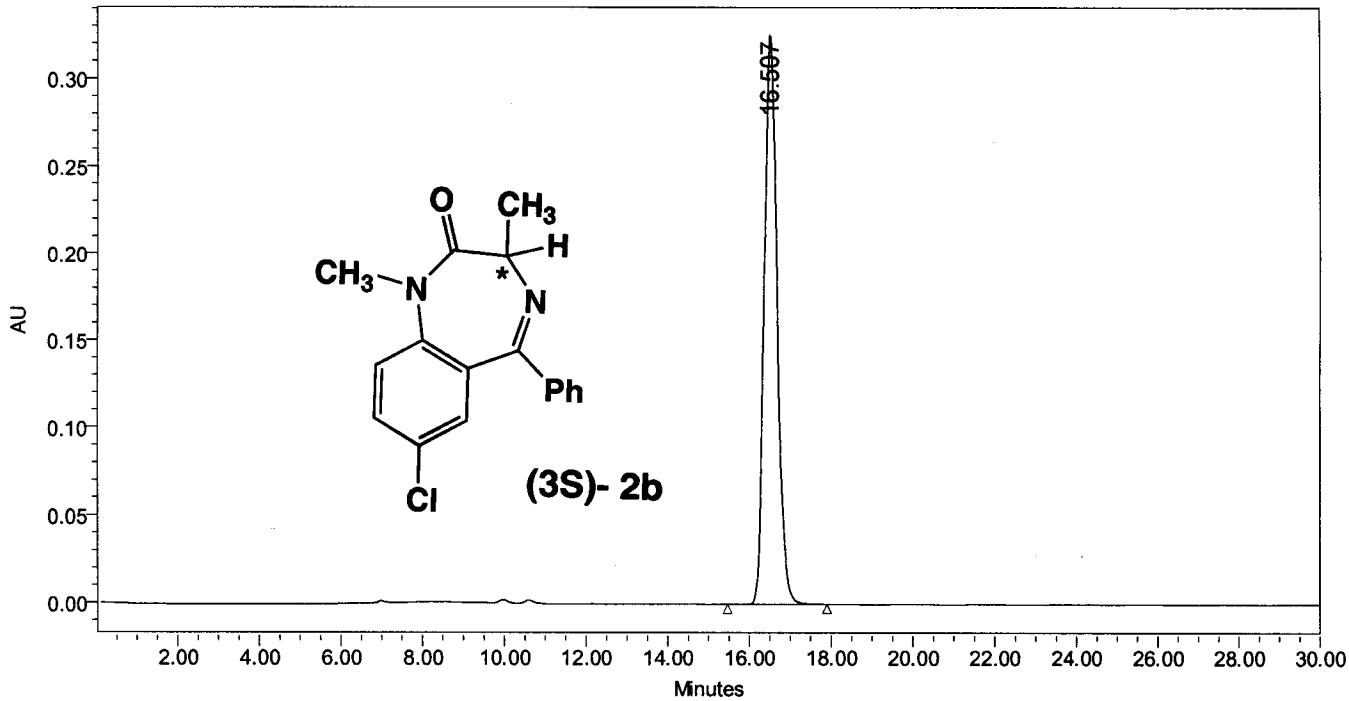


	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	14.663	8608993	50.02	432337	52.28
2	16.547	8603447	49.98	394697	47.72

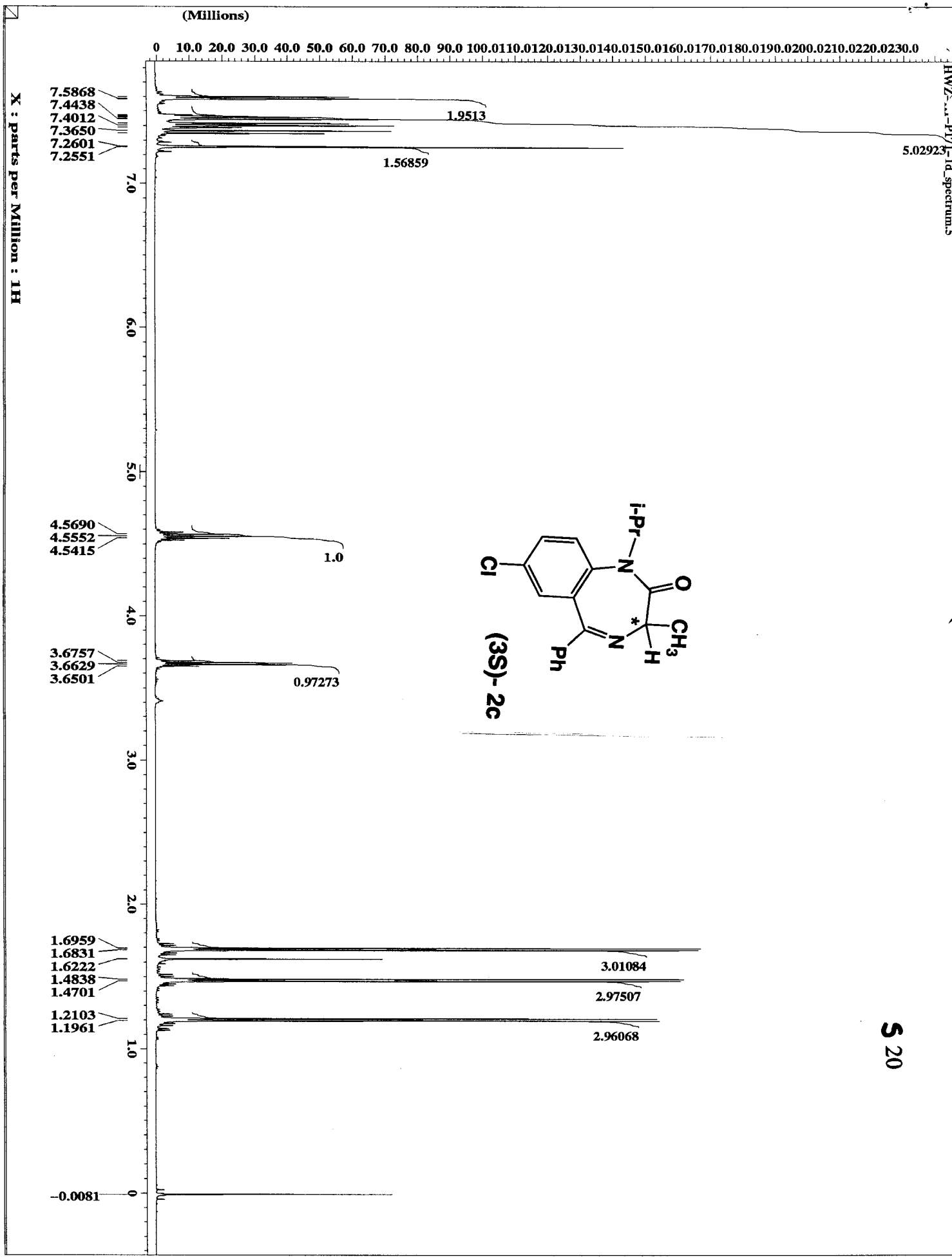
Project Name: HONGWU
Reported by User: JOE

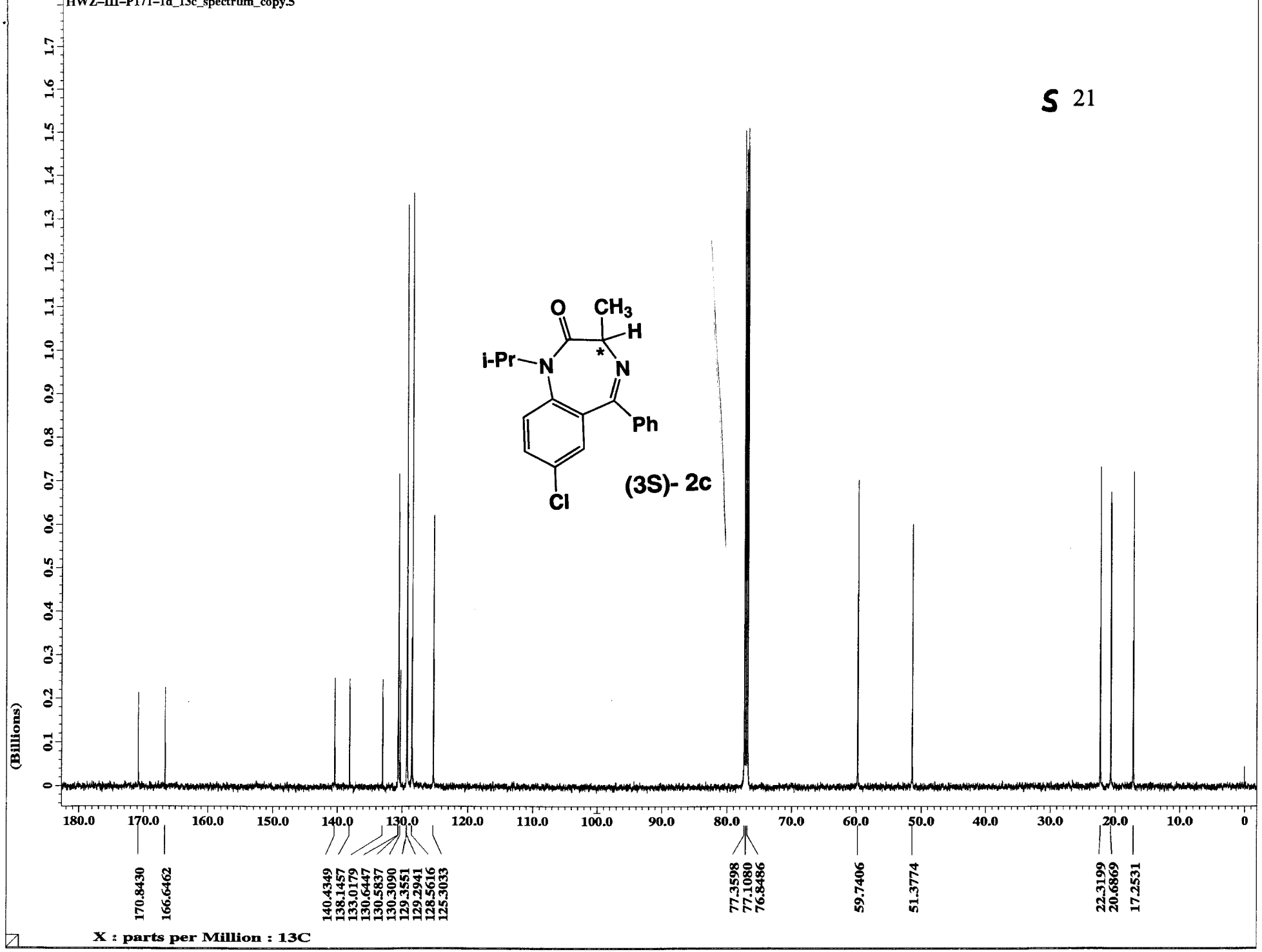
SAMPLE INFORMATION

Sample Name:	HWZ-III-P121	Acquired By:	HongWu
Sample Type:	Unknown	Date Acquired:	3/13/03 1:00:03 PM
Vial:	1	Acq. Method:	5%B Isopropanol
Injection #:	1	Date Processed:	3/13/03 1:58:04 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	30.00 Minutes	Sample Set Name:	Hongwu



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	16.507	7107896	100.00	325693	100.00

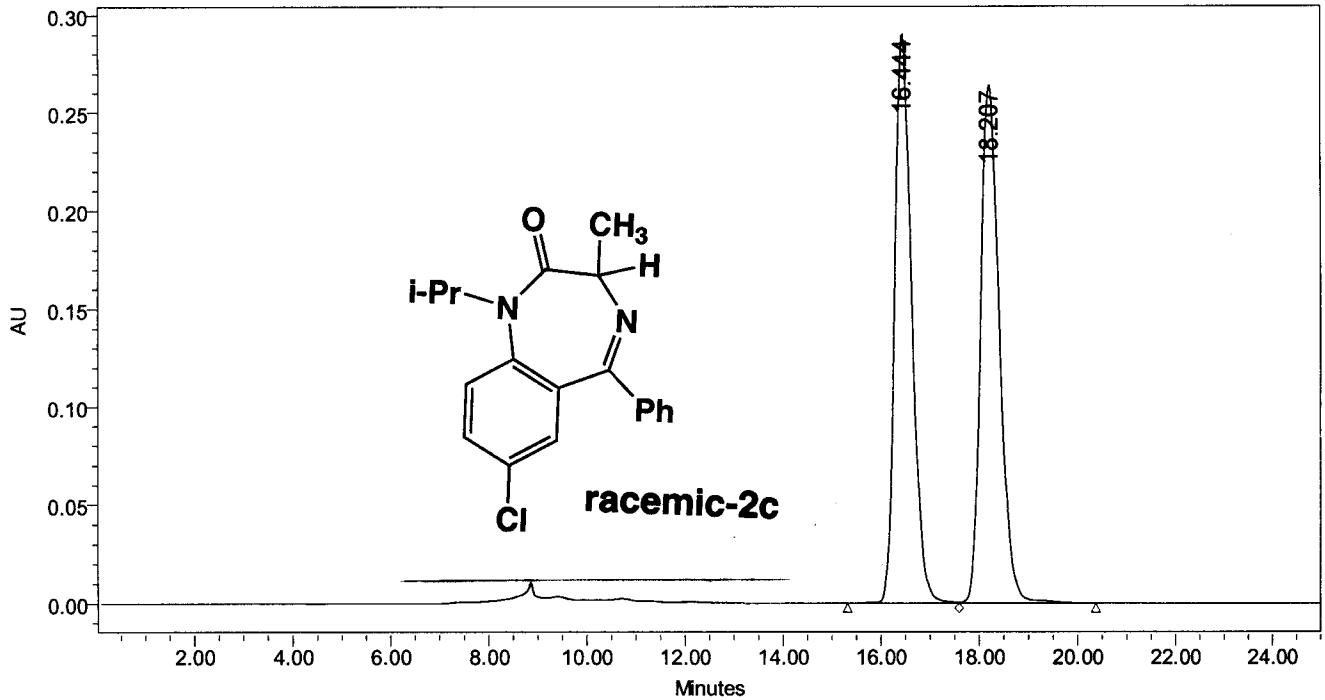

(Millions)
0 10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0 100.0 110.0 120.0 130.0 140.0 150.0 160.0 170.0 180.0 190.0 200.0 210.0 220.0 230.0
X : parts per Million : 1H
7.5868
7.4438
7.4012
7.3650
7.2601
7.2551
1.9513
5.02923
1.56859
4.5690
4.5552
4.5415
1.0
3.6757
3.6629
3.6501
0.97273
1.6959
1.6831
1.6222
1.4838
1.4701
3.01084
2.97507
1.2103
1.1961
2.96068
−0.0081
i-Pr
N
O
CH3
H
N
Ph
Cl
(3S)- 2c


HWZ-III-P171-1d_13c_spectrum_copy.5
(Billions)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
O
CH3
H
i-Pr
N
*
N
Ph
Cl
(3S)- 2c
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.8430
166.6462
140.4349
138.1457
133.0179
130.6447
130.5837
130.3090
129.3551
129.2941
128.5616
125.3033
77.3598
77.1080
76.8486
59.7406
51.3774
22.3199
20.6869
17.2531
X : parts per Million : 13C

Project Name: HONGWU
Reported by User: JOE

SAMPLE INFORMATION

Sample Name:	HWZ-II-P161	Acquired By:	HongWu
Sample Type:	Unknown	Date Acquired:	2/26/03 12:23:29 PM
Vial:	1	Acq. Method:	1%B
Injection #:	1	Date Processed:	2/26/03 12:48:43 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	25.00 Minutes	Sample Set Name:	Hongwu

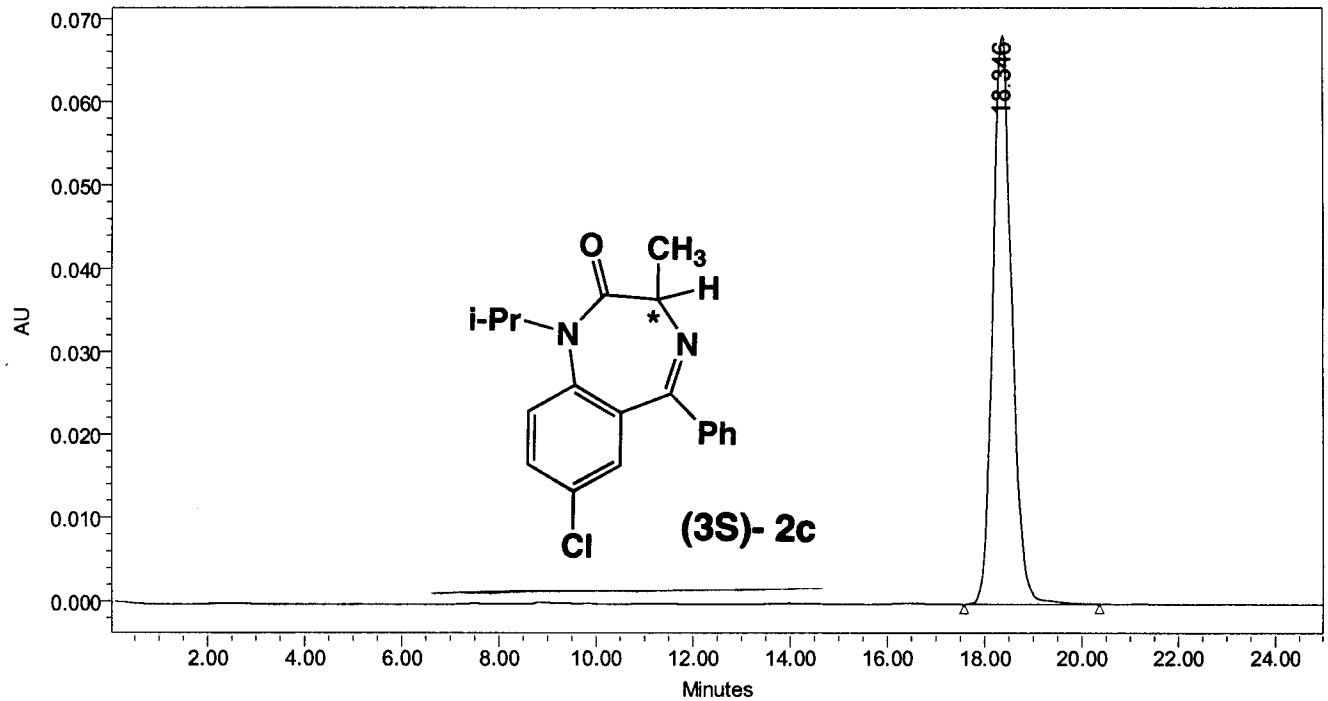


	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	16.444	6947419	49.90	289950	52.36
2	18.207	6975494	50.10	263840	47.64

Project Name: HONGWU
Reported by User: JOE

SAMPLE INFORMATION

Sample Name:	HWZ-III-P109	Acquired By:	HongWu
Sample Type:	Unknown	Date Acquired:	2/26/03 11:32:02 AM
Vial:	1	Acq. Method:	1%B
Injection #:	1	Date Processed:	2/26/03 11:57:16 AM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	25.00 Minutes	Sample Set Name:	Hongwu



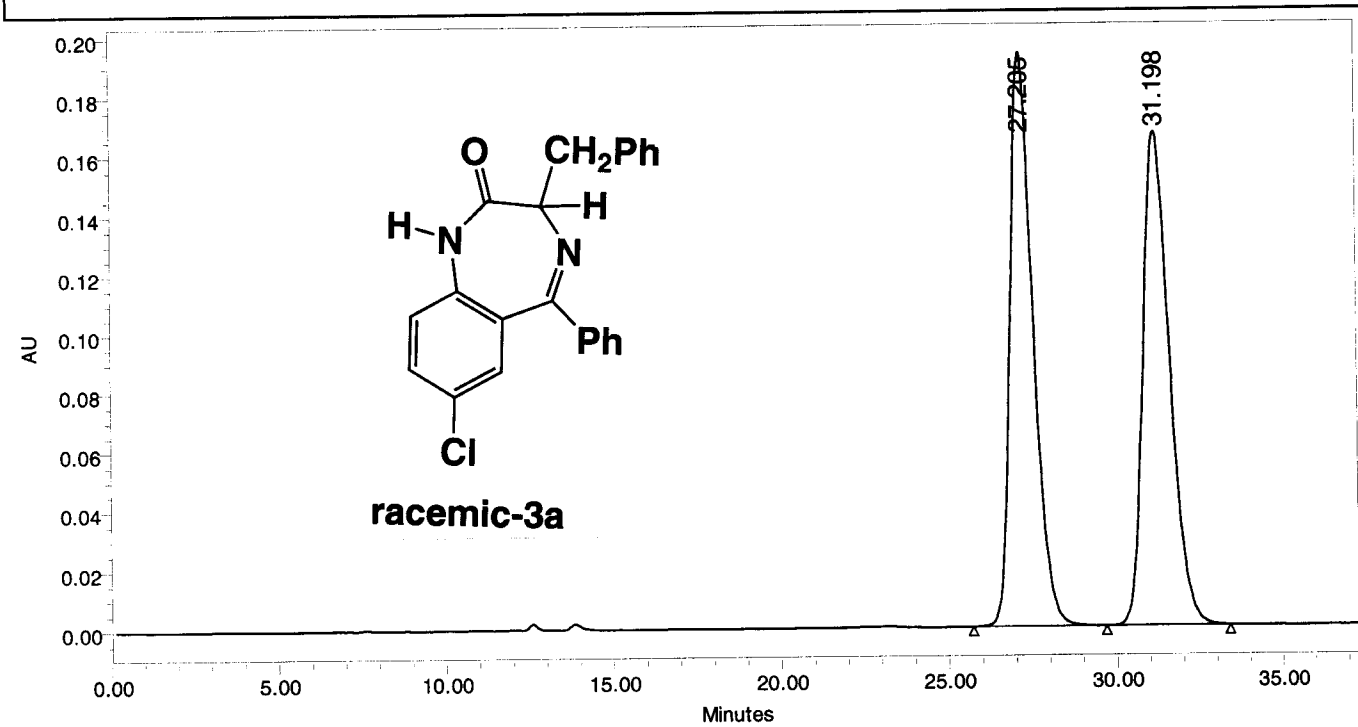
	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	18.346	1849662	100.00	68272	100.00

Project Name: Joe_Chiral
Reported by User: JOE

S 24 Breeze

SAMPLE INFORMATION

Sample Name:	JCD-II-73	Acquired By:	JOE
Sample Type:	Unknown	Date Acquired:	2/7/03 4:21:48 PM
Vial:	1	Acq. Method:	3% B
Injection #:	1	Date Processed:	2/7/03 5:44:12 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	40.00 Minutes	Sample Set Name:	JOE



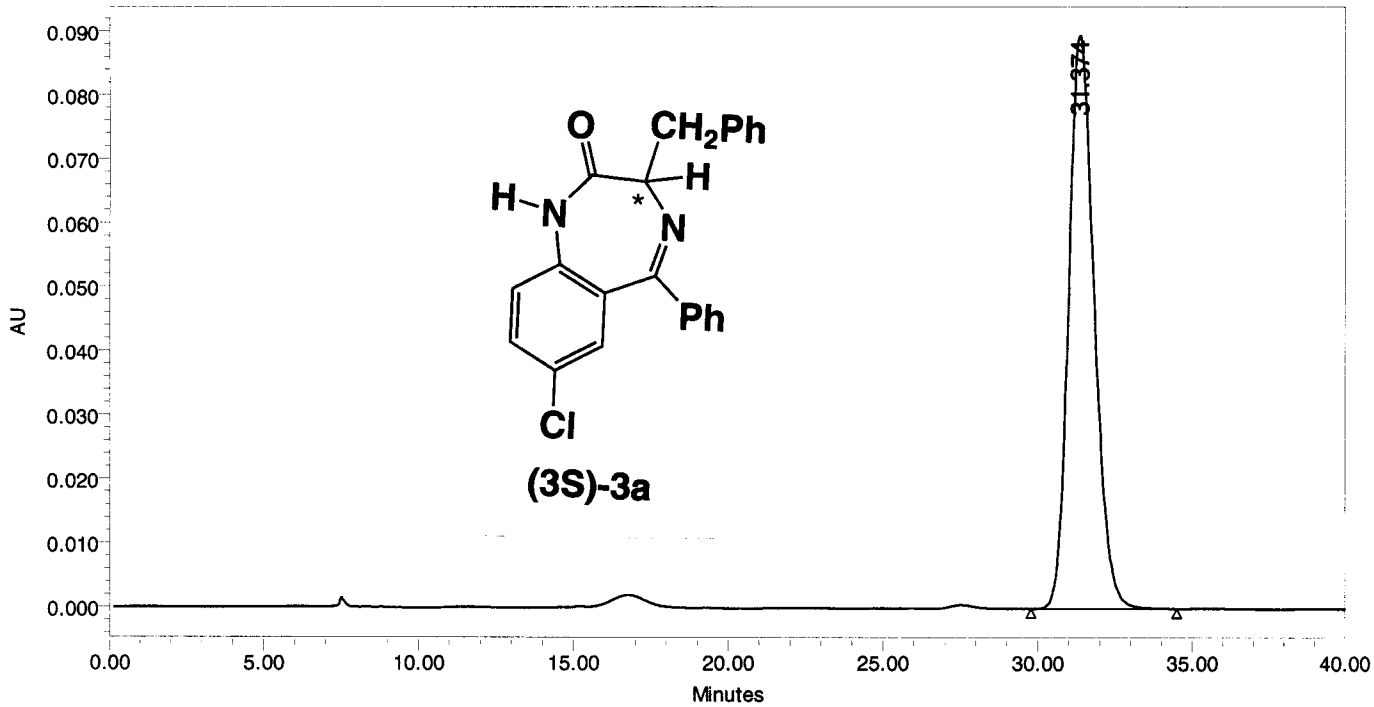
	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	27.205	9158208	49.86	193589	53.77
2	31.198	9209905	50.14	166470	46.23

Project Name: Joe_Chiral
Reported by User: JOE

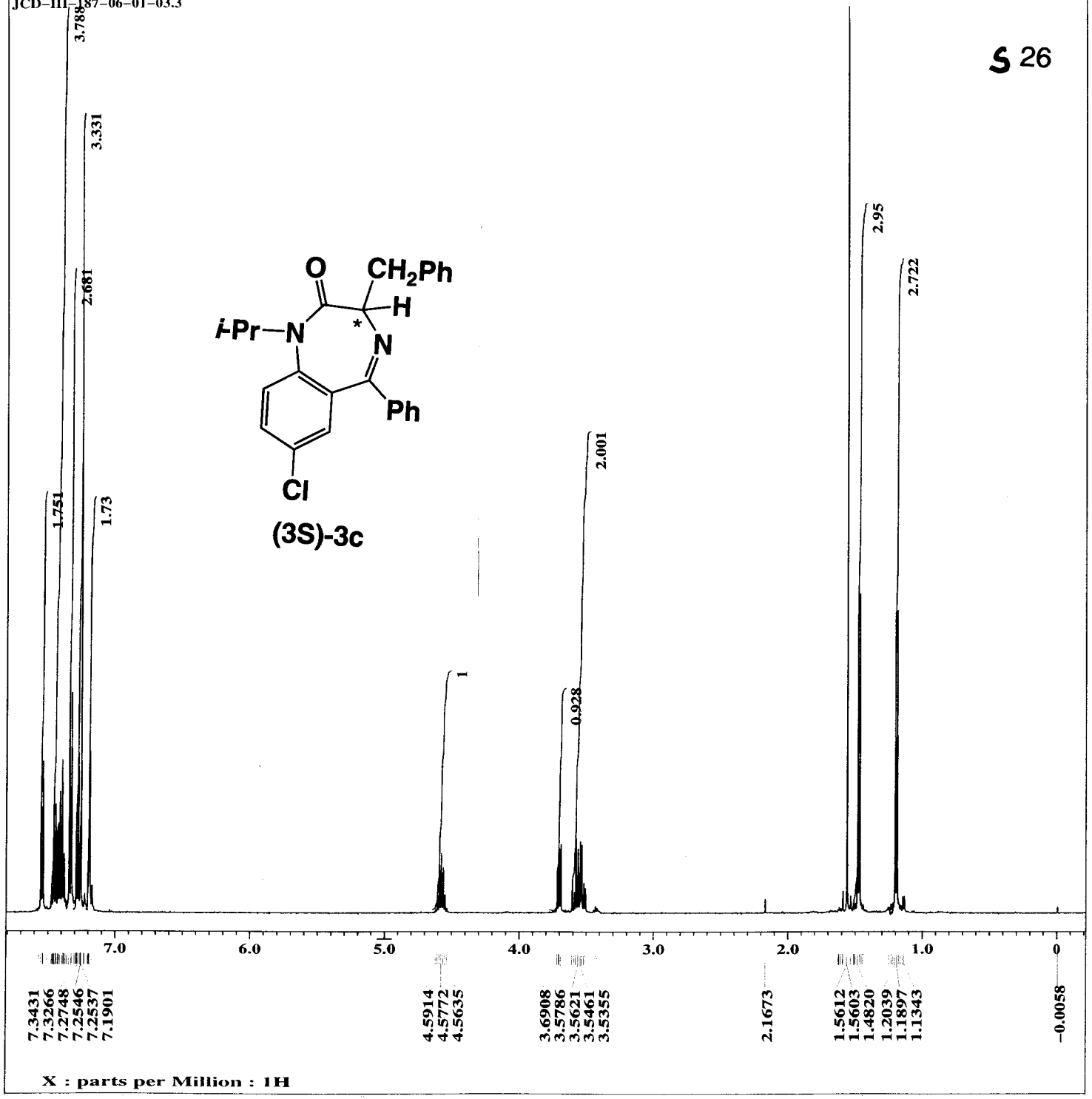
S 25 Breeze

SAMPLE INFORMATION

Sample Name:	JCD-III-120(6-10)	Acquired By:	JOE
Sample Type:	Unknown	Date Acquired:	2/7/03 5:02:03 PM
Vial:	1	Acq. Method:	3% B
Injection #:	1	Date Processed:	2/7/03 5:42:20 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	40.00 Minutes	Sample Set Name:	JOE



	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	31.374	5110168	100.00	89533	100.00

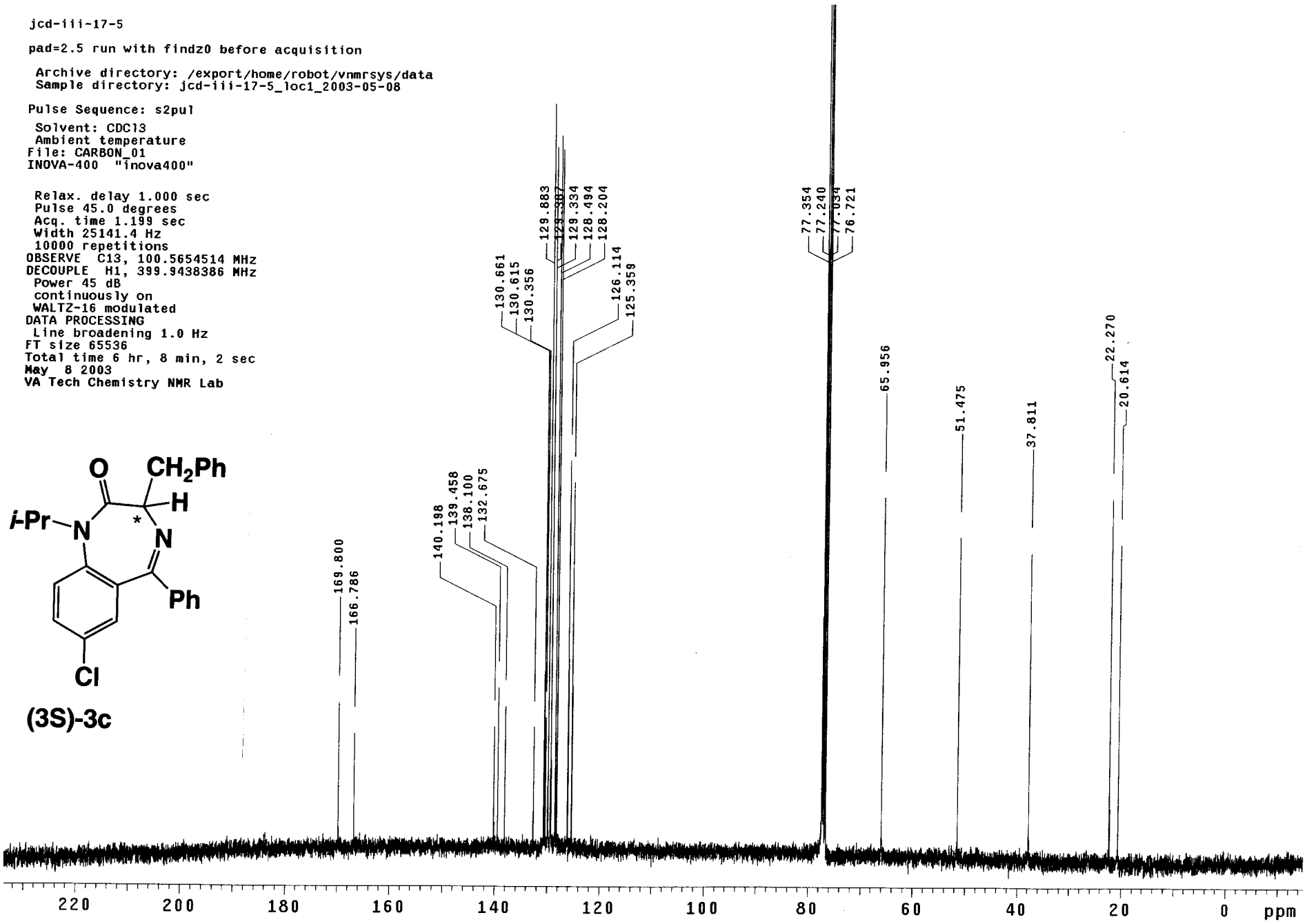


---- ACQUISITION PARAMETERS ----
Derived from: JCD-III-187-06-01-03.1
File Name = JCD-III-187-06-01-03.
Author = carlier
Sample ID = JCD-III-187-06-01-03
Content = Single Pulse Experime
Creation Date = 1-JUN-2003 19:19:20

Revision Date = 4-JUN-2003 13:53:35
Spec Site = Eclipse+ 500

Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 1H
Dim Size = 32768
Dim Units = [ppm]
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 32
Total_scans = 32

X_90_width = 11.5[us]
X_acq_time = 4.3646976[s]
X_angle = 30[deg]
X_pulse = 3.83333333[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Relaxation_delay = 1[s]
Unblank_time = 2[us]

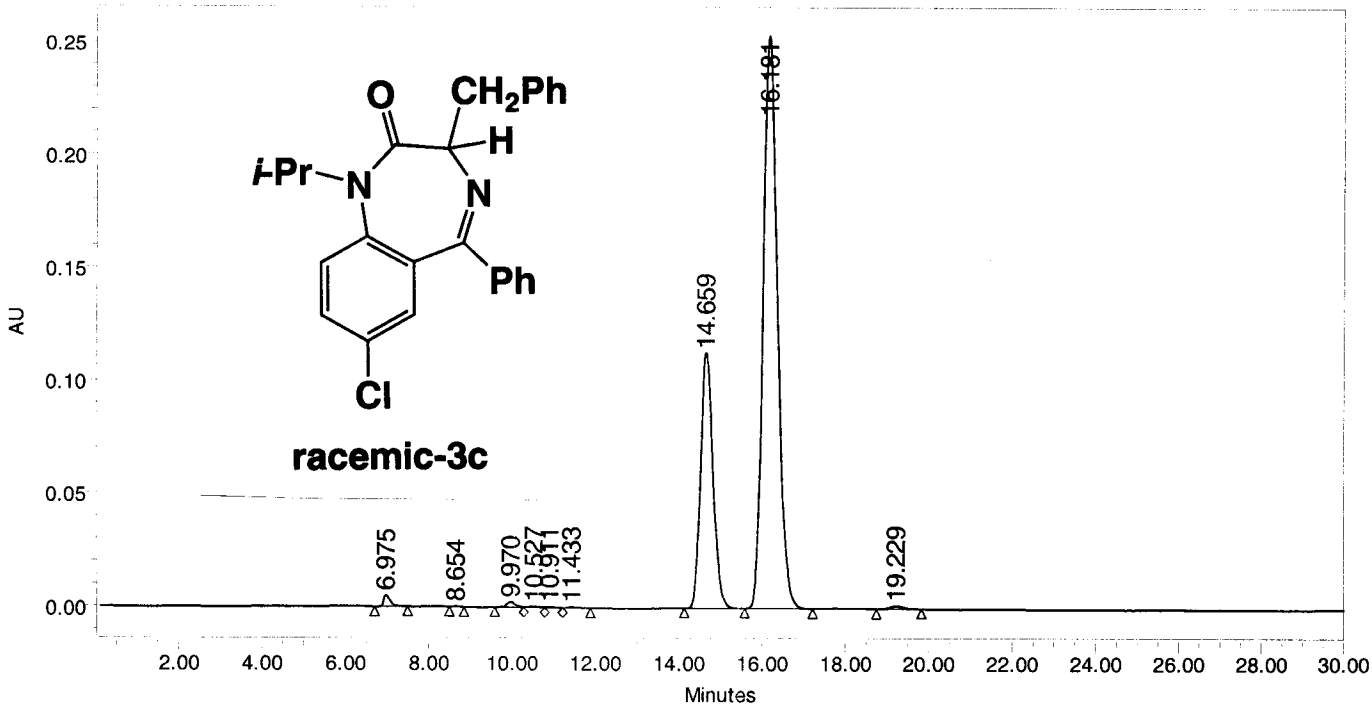

jcd-iii-17-5
pad=2.5 run with findz0 before acquisition
Archive directory: /export/home/robot/vnmrsys/data
Sample directory: jcd-iii-17-5_loc1_2003-05-08
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: CARBON_01
INOVA-400 "inova400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25141.4 Hz
10000 repetitions
OBSERVE C13, 100.5654514 MHz
DECOUPLE H1, 399.9438386 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 6 hr, 8 min, 2 sec
May 8 2003
VA Tech Chemistry NMR Lab
O
CH2Ph
H
i-Pr
N
*
N
Ph
Cl
(3S)-3c
169.800
166.786
140.198
139.458
138.100
132.675
130.661
130.615
130.356
129.883
129.387
129.334
128.494
128.204
126.114
125.359
77.354
77.240
77.034
76.721
65.956
51.475
37.811
22.270
20.614
220
200
180
160
140
120
100
80
60
40
20
0
ppm

Project Name: Joe_Chiral
Reported by User: JOE

S 28 Breeze

SAMPLE INFORMATION

Sample Name:	JCD-III-159-175AD	Acquired By:	JOE
Sample Type:	Unknown	Date Acquired:	4/24/03 12:35:25 PM
Vial:	1	Acq. Method:	5% B
Injection #:	1	Date Processed:	4/24/03 1:25:06 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	30.00 Minutes	Sample Set Name:	JOE



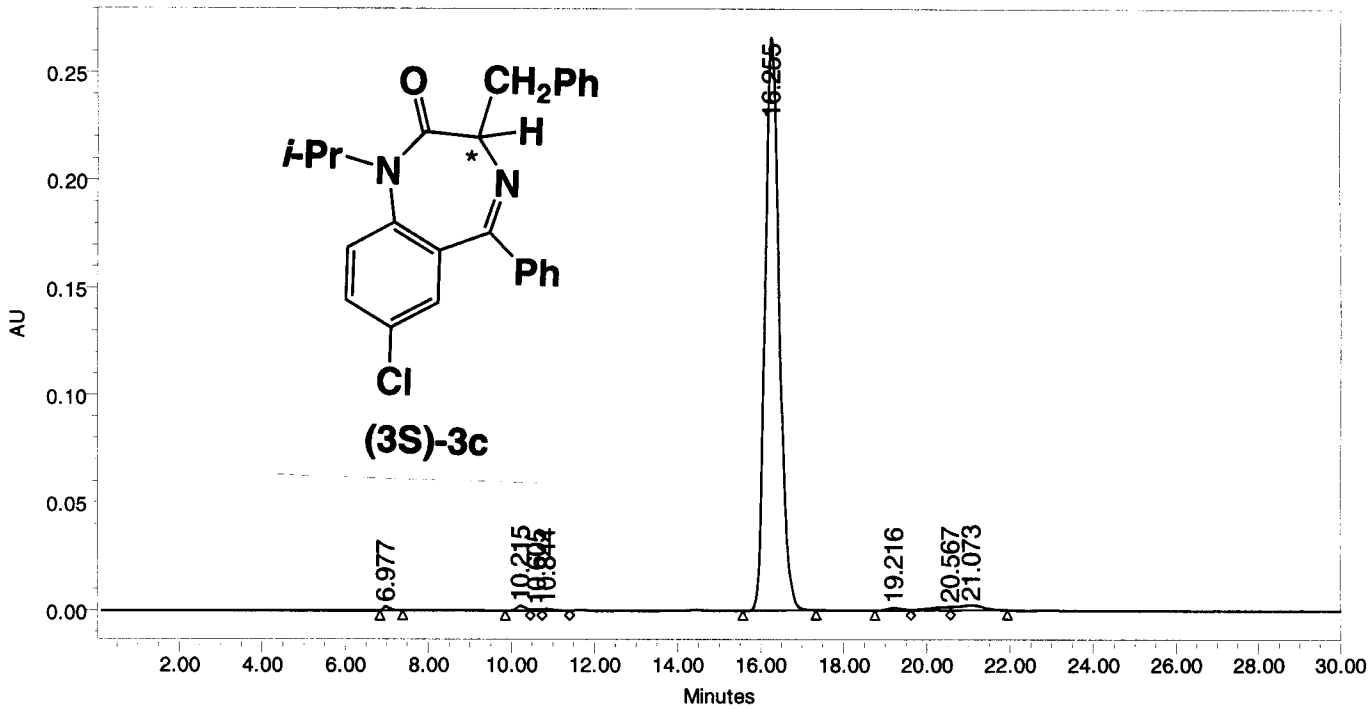
	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	6.975	54925	0.64	5048	1.34
2	8.654	2833	0.03	294	0.08
3	9.970	35070	0.41	2307	0.61
4	10.527	11620	0.14	532	0.14
5	10.911	5919	0.07	402	0.11
6	11.433	6398	0.07	342	0.09
7	14.659	2340778	27.43	113126	30.00
8	16.181	6046821	70.86	253754	67.30
9	19.229	29593	0.35	1270	0.34

Project Name: Joe_Chiral
Reported by User: JOE

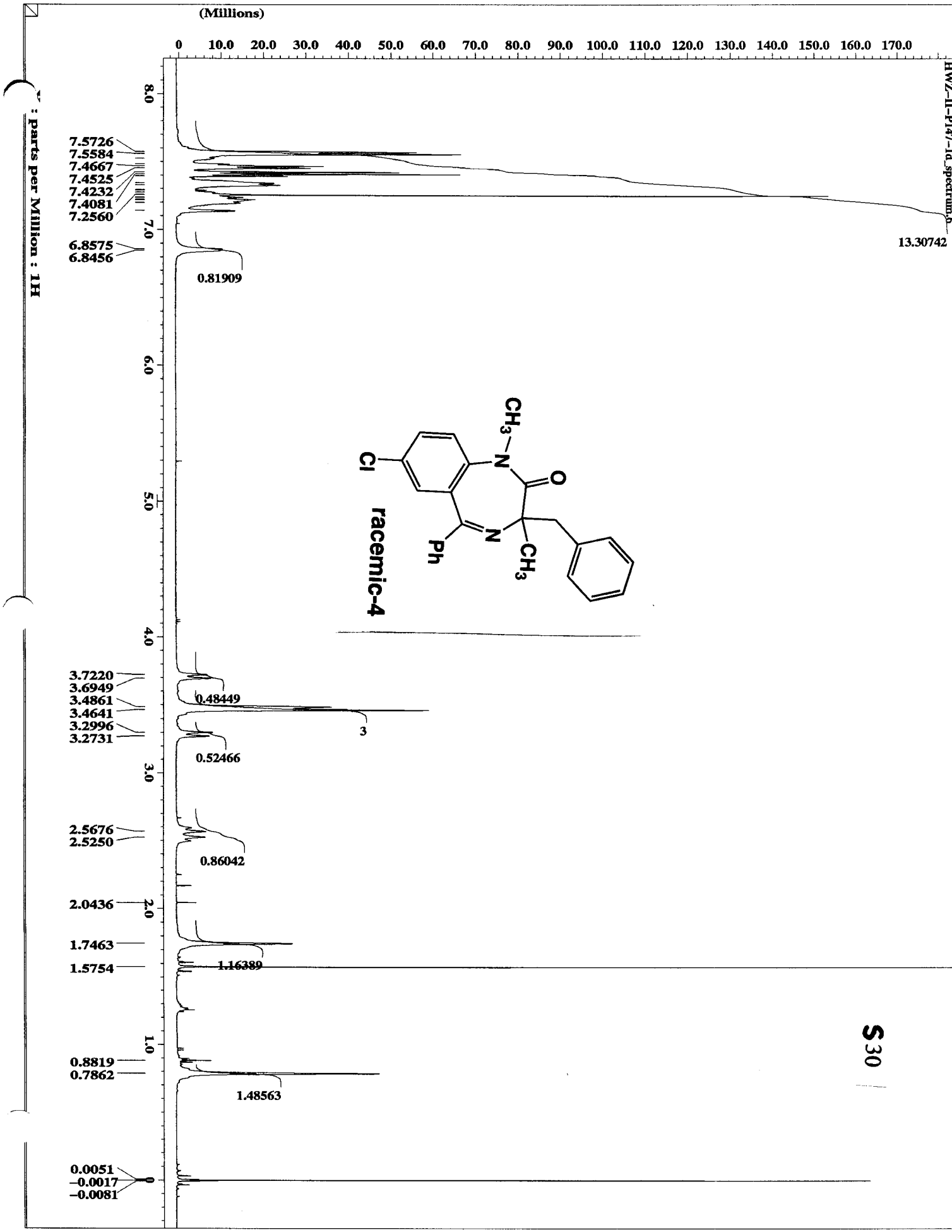
S29 Breeze

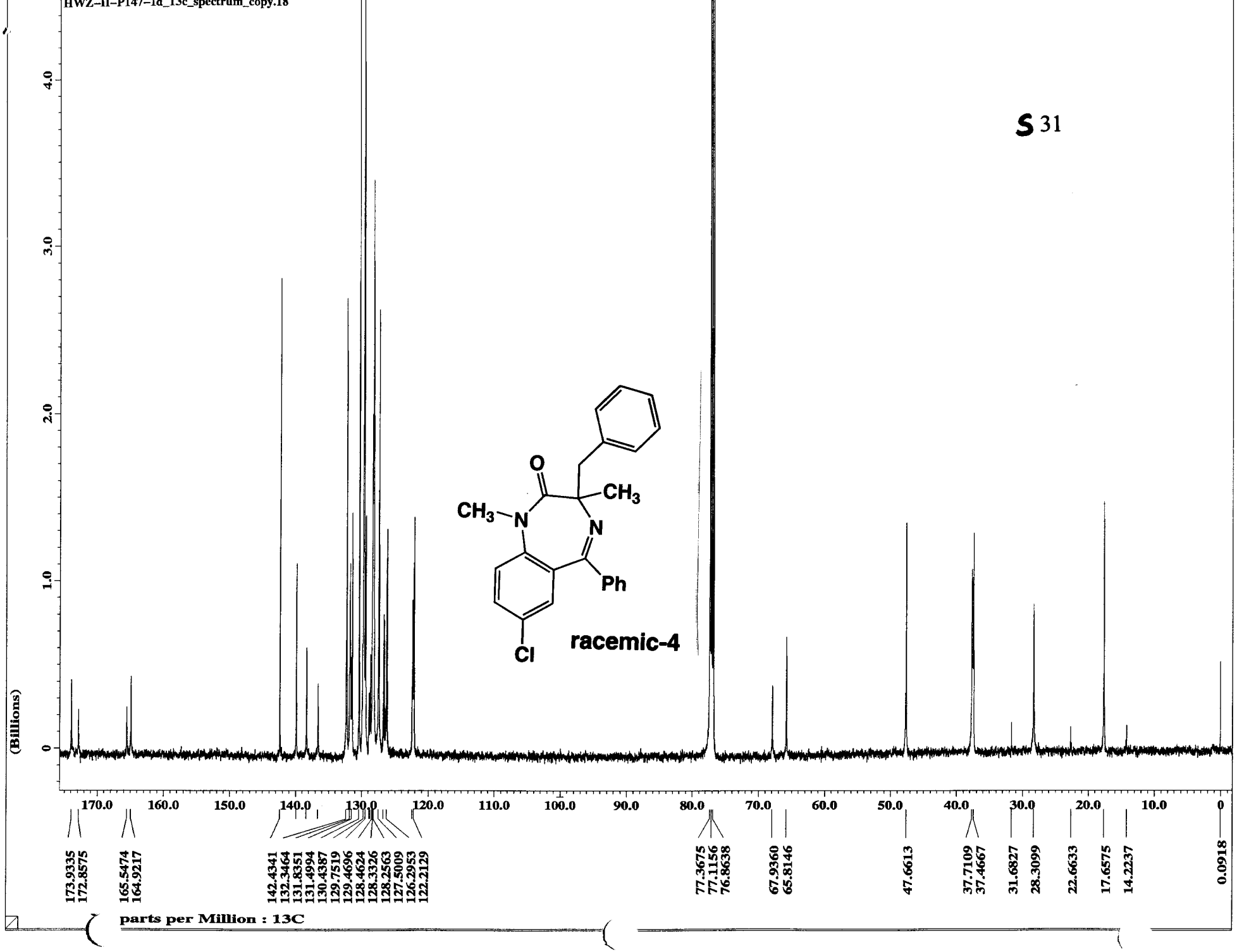
SAMPLE INFORMATION

Sample Name:	JCD-III-159AD	Acquired By:	JOE
Sample Type:	Unknown	Date Acquired:	3/28/03 1:28:14 PM
Vial:	2	Acq. Method:	5% B
Injection #:	1	Date Processed:	6/9/03 1:38:58 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	30.00 Minutes	Sample Set Name:	JOE



	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	6.977	20358	0.31	1870	0.67
2	10.215	33601	0.51	2252	0.81
3	10.605	13001	0.20	823	0.30
4	10.844	15064	0.23	843	0.30
5	16.255	6325619	95.80	266783	96.02
6	19.216	29933	0.45	1234	0.44
7	20.567	57192	0.87	1643	0.59
8	21.073	108410	1.64	2400	0.86


(Millions)
0 10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0 100.0 110.0 120.0 130.0 140.0 150.0 160.0 170.0
HWZ-II-P147-1d_spectrum.0
: parts per Million : 1H
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.5726
7.5584
7.4667
7.4525
7.4232
7.4081
7.2560
6.8575
6.8456
0.81909
13.30742
racemic-4
Cl
CH3
N
O
N
Ph
CH3
3.7220
3.6949
3.4861
3.4641
3.2996
3.2731
0.48449
3
0.52466
2.5676
2.5250
0.86042
2.0436
1.7463
1.5754
1.16389
0.8819
0.7862
1.48563
0.0051
−0.0017
−0.0081

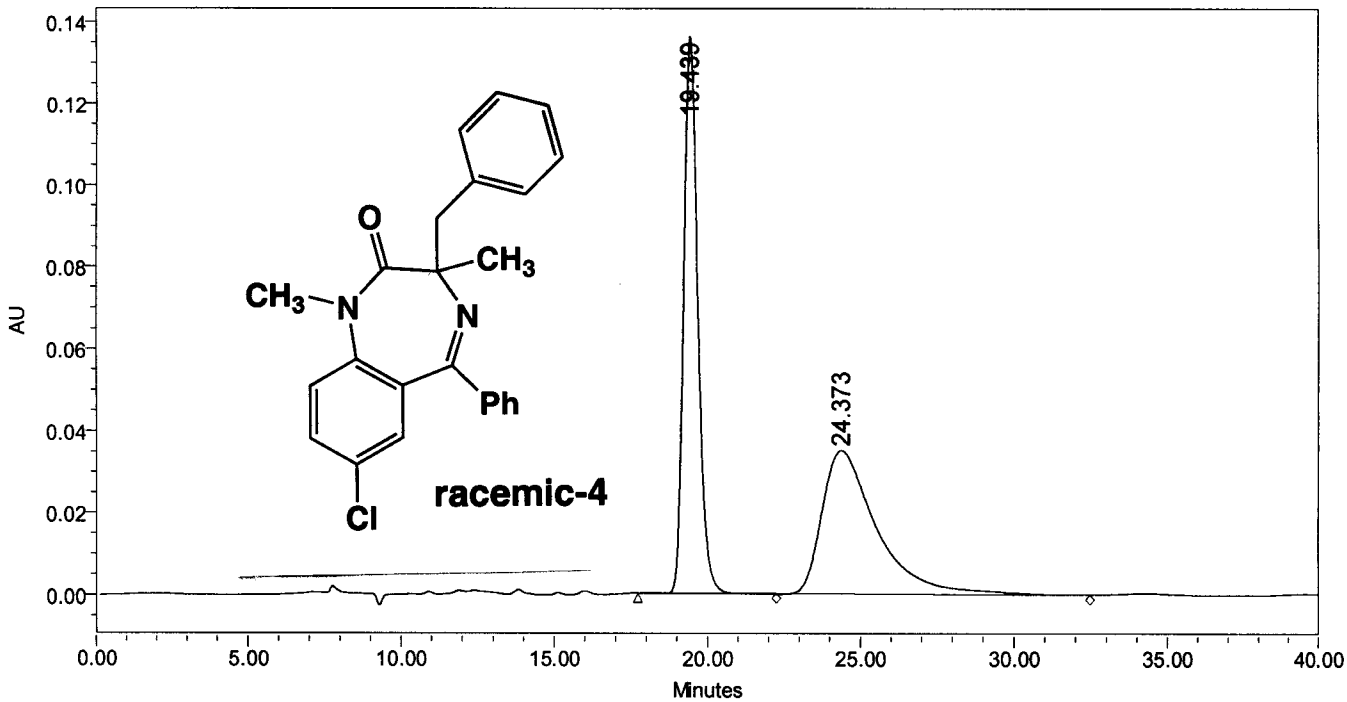

HWZ-II-P147-1d_13c_spectrum_copy.18
racemic-4
(Billions)
parts per Million : 13C
173.9335
172.8575
165.5474
164.9217
142.4341
132.3464
131.8351
131.4994
130.4387
129.7519
129.4696
128.4624
128.3326
128.2563
127.5009
126.2953
122.2129
77.3675
77.1156
76.8638
67.9360
65.8146
47.6613
37.7109
37.4667
31.6827
28.3099
22.6633
17.6575
14.2237
0.0918

Project Name: HONGWU
Reported by User: JOE

S 32

SAMPLE INFORMATION

Sample Name:	HWZ-II-P147-AD-H	Acquired By:	HongWu
Sample Type:	Unknown	Date Acquired:	5/2/03 2:25:30 PM
Vial:	1	Acq. Method:	2%B
Injection #:	1	Date Processed:	6/6/03 5:45:34 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	40.00 Minutes	Sample Set Name:	Hongwu

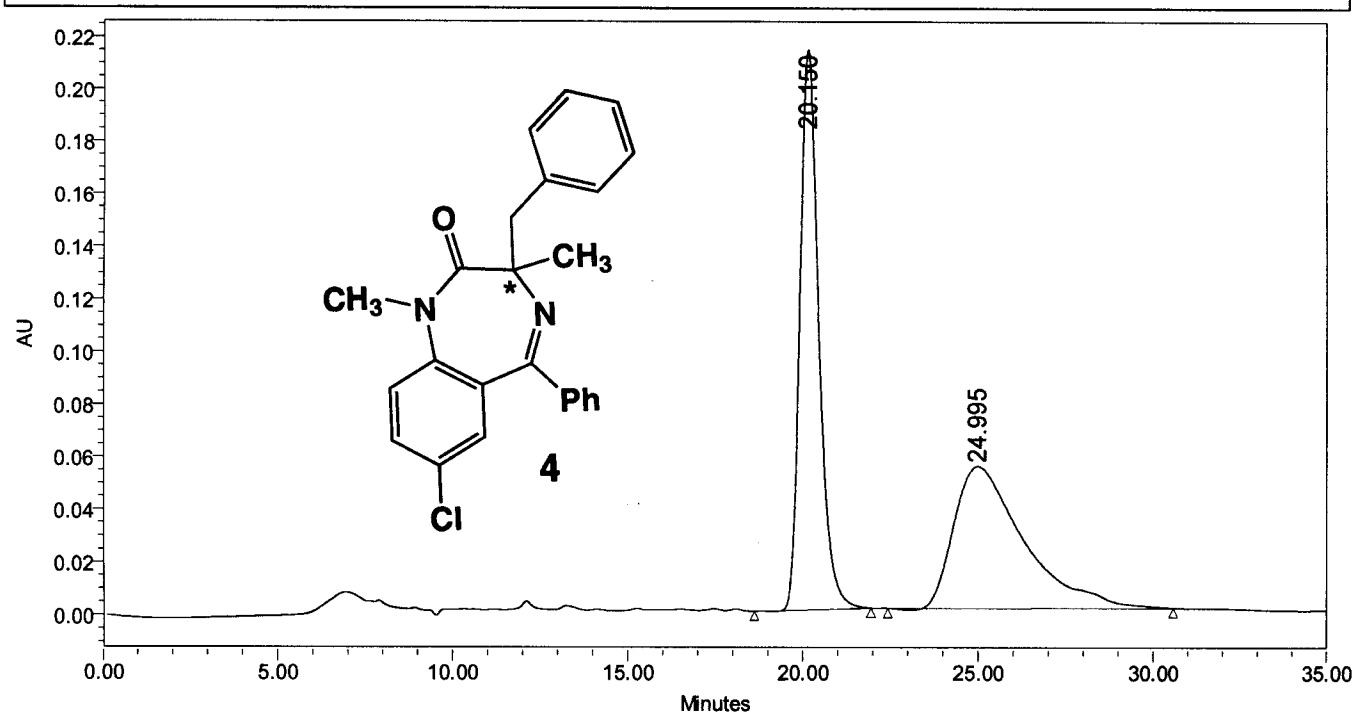


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	19.439	4373175	50.23	135999	79.50
2	24.373	4332324	49.77	35069	20.50

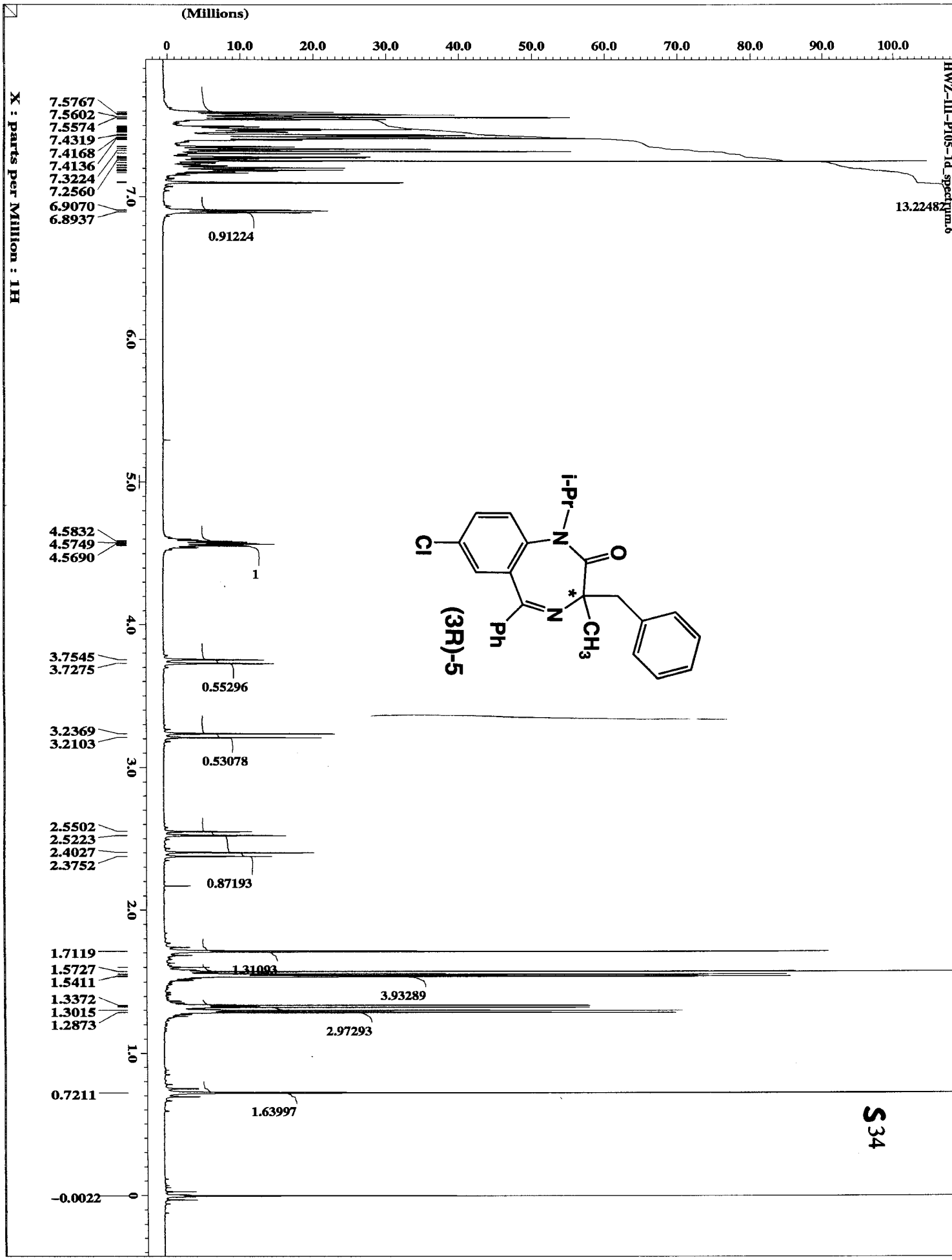
Project Name: HONGWU
Reported by User: HongWu

SAMPLE INFORMATION

Sample Name:	HWZ-IV-P18-AD-H	Acquired By:	HongWu
Sample Type:	Unknown	Date Acquired:	5/2/03 5:46:07 PM
Vial:	1	Acq. Method:	2%B
Injection #:	1	Date Processed:	5/2/03 6:32:28 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	35.00 Minutes	Sample Set Name:	Hongwu



	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	20.150	7971859	51.69	213123	79.83
2	24.995	7450687	48.31	53841	20.17


(Millions)
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
HWZ-III-P105-1d_spectrum.6
X : parts per Million : 1H
7.5767
7.5602
7.5574
7.4319
7.4168
7.4136
7.3224
7.2560
6.9070
6.8937
13.22482
0.91224
4.5832
4.5749
4.5690
1
3.7545
3.7275
0.55296
3.2369
3.2103
0.53078
2.5502
2.5223
2.4027
2.3752
0.87193
1.7119
1.5727
1.5411
1.31093
3.93289
1.3372
1.3015
1.2873
2.97293
0.7211
1.63997
−0.0022
i-Pr
N
O
Cl
*
N
Ph
CH3
(3R)-5

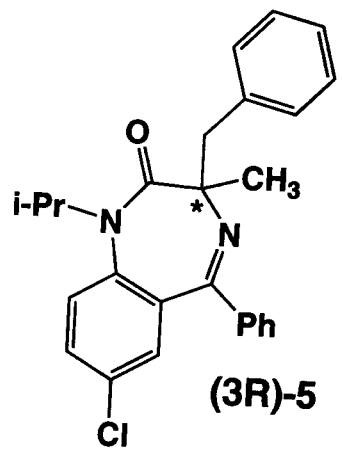
lch-xii-115-2

pad=2.5 run with findz0 before acquisition

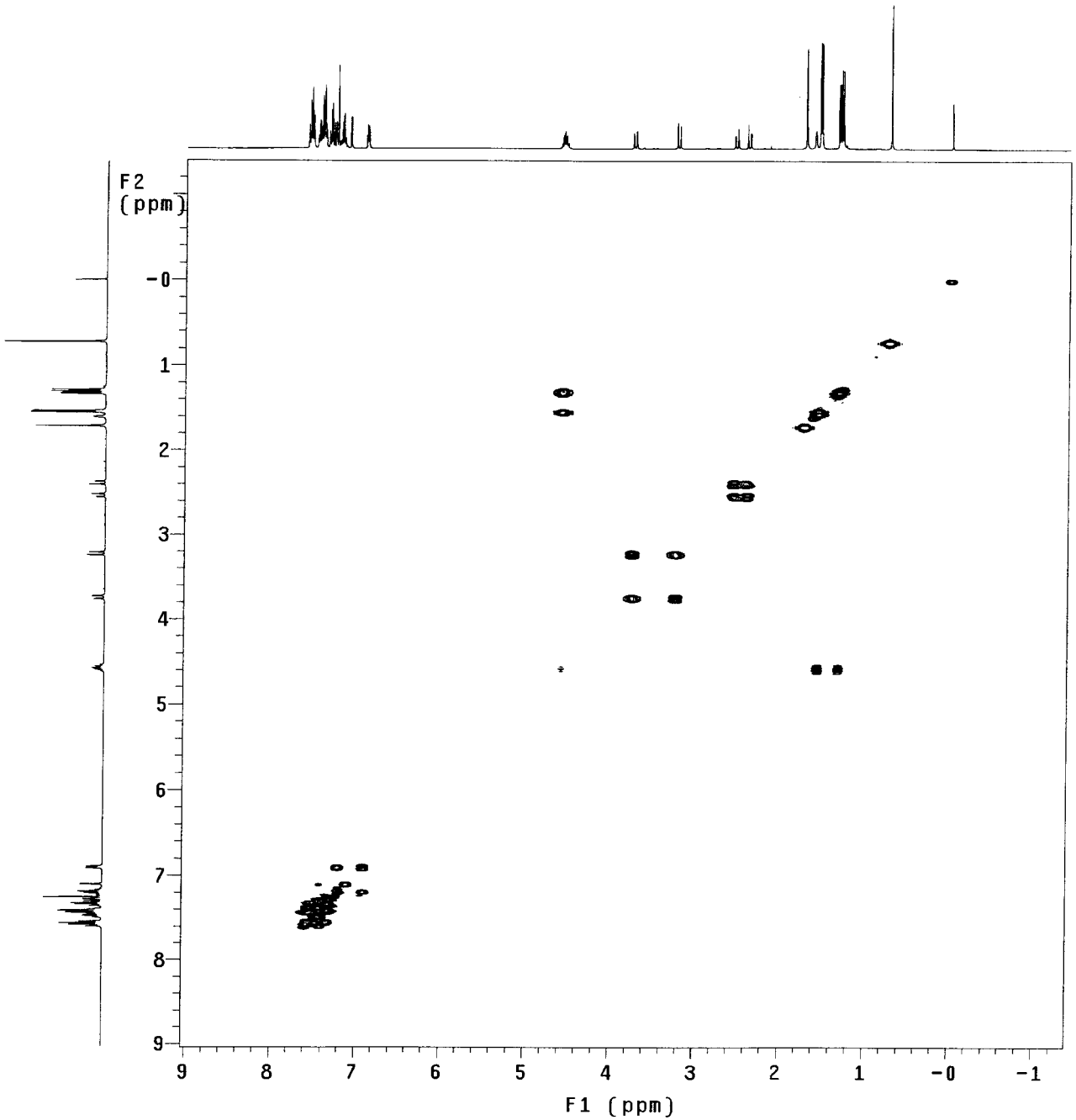
Archive directory: /export/home/robot/vnmrsys/data
Sample directory: lch-xii-115-2_loc3_2003-06-04

Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
File: gCOSY_01
INOVA-400 "inova400"

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4174.9 Hz
2D Width 4174.9 Hz
2 repetitions
128 increments
OBSERVE H1, 399.9418409 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.031 sec
FT size 2048 x 2048
Total time 5 min, 20 sec
Jun 4 2003
VA Tech Chemistry NMR Lab



(3R)-5



lch-xii-115-2

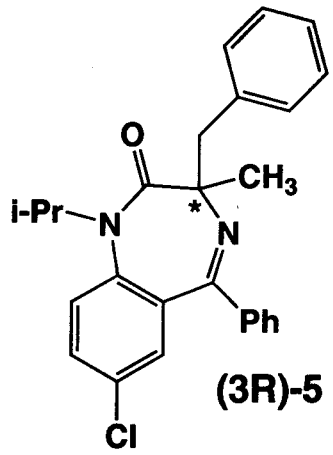
pad=2.5 run with findz0 before acquisition

Archive directory: /export/home/robot/vnmrsys/data
Sample directory: lch-xii-115-2_loc3_2003-06-04

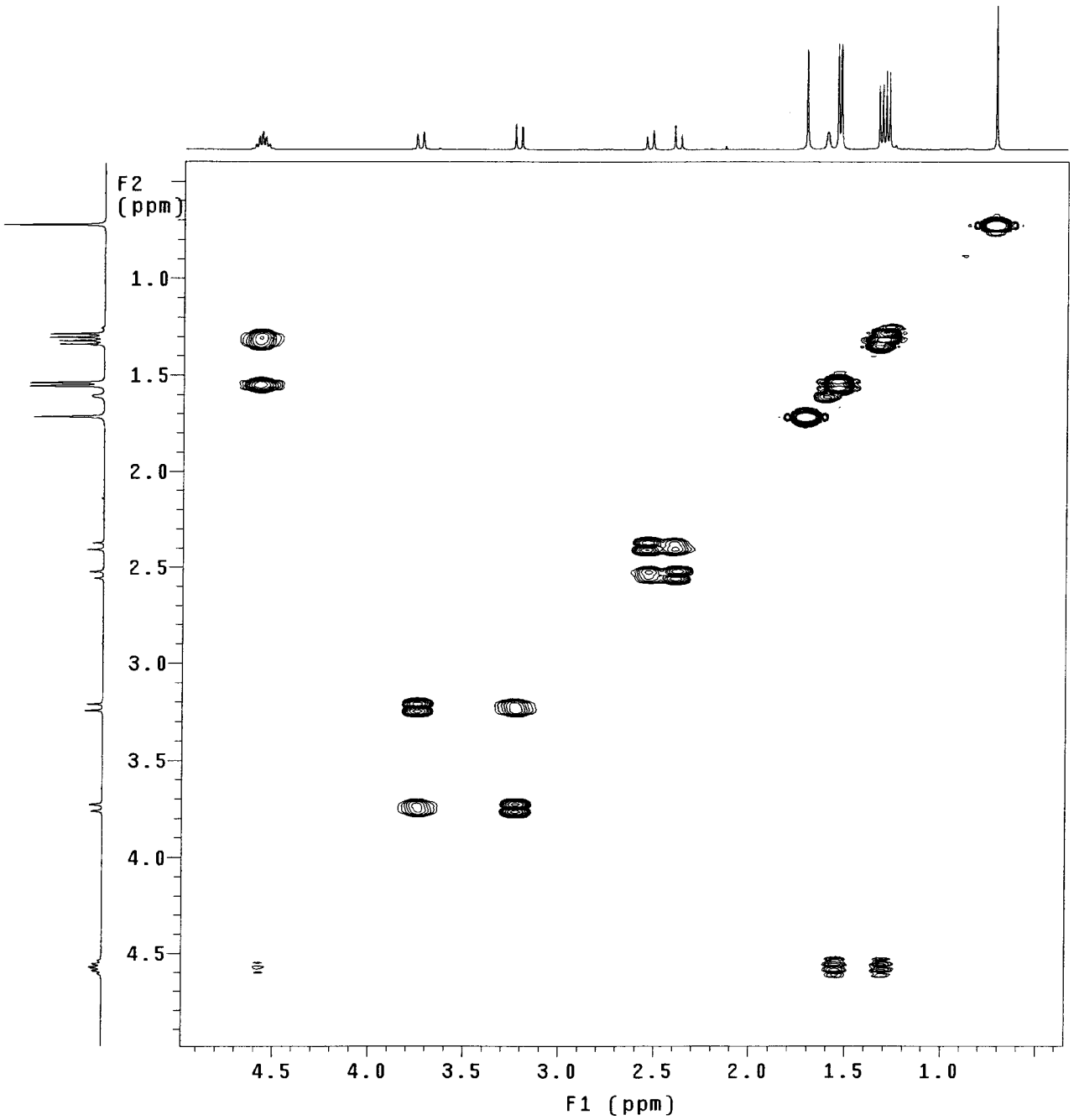
Pulse Sequence: gCOSY

Solvent: CDCl3
Ambient temperature
File: gCOSY_01
INOVA-400 "inova400"

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4174.9 Hz
2D Width 4174.9 Hz
2 repetitions
128 increments
OBSERVE H1, 399.9418409 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.031 sec
FT size 2048 x 2048
Total time 5 min, 20 sec
Jun 4 2003
VA Tech Chemistry NMR Lab



(3R)-5

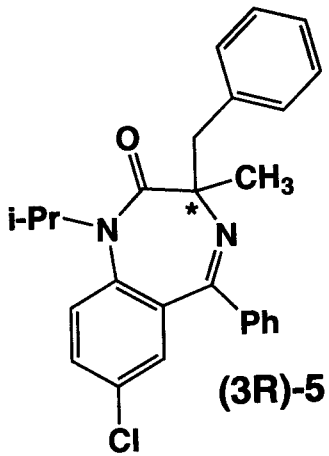


lch-xii-115-2

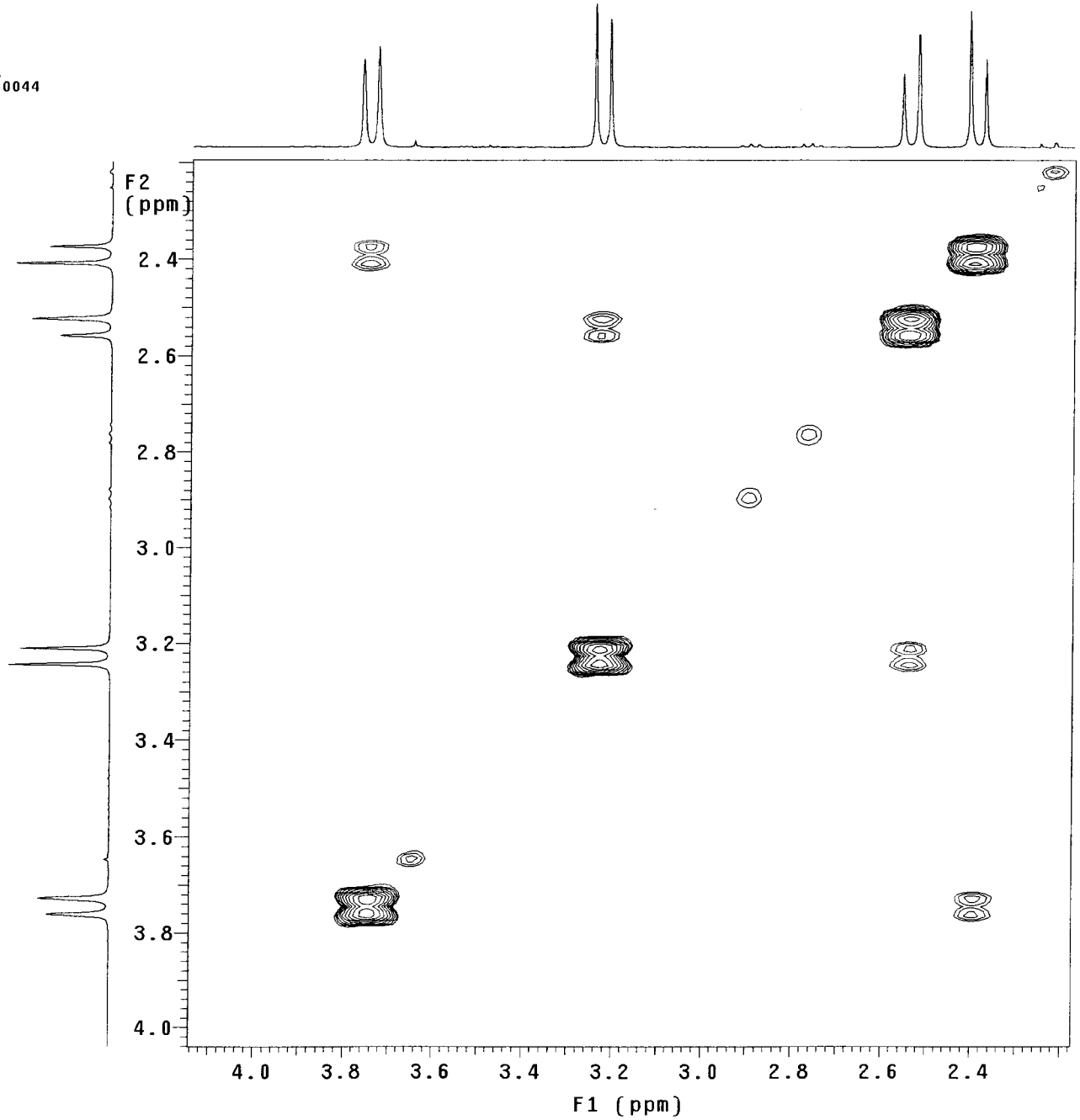
Archive directory: /export/home/robot/vnmrsys/data
Sample directory: lch-xii-115-2_1oc3_2003-06-04-180044

Pulse Sequence: NOESY
Solvent: CDCl3
Ambient temperature
File: NOESY_01
INOVA-400 "inova400"

Relax. delay 2.000 sec
Mixing 1.000 sec
Acq. time 0.150 sec
Width 4174.9 Hz
2D Width 4174.9 Hz
4 repetitions
2 x 128 increments
OBSERVE H1, 399.9418406 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.028 sec
FT size 2048 x 2048
Total time 55 min, 56 sec
Jun 4 2003
VA Tech Chemistry NMR Lab



(3R)-5

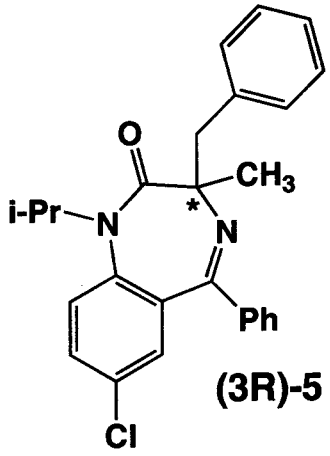


lch-xii-115-2

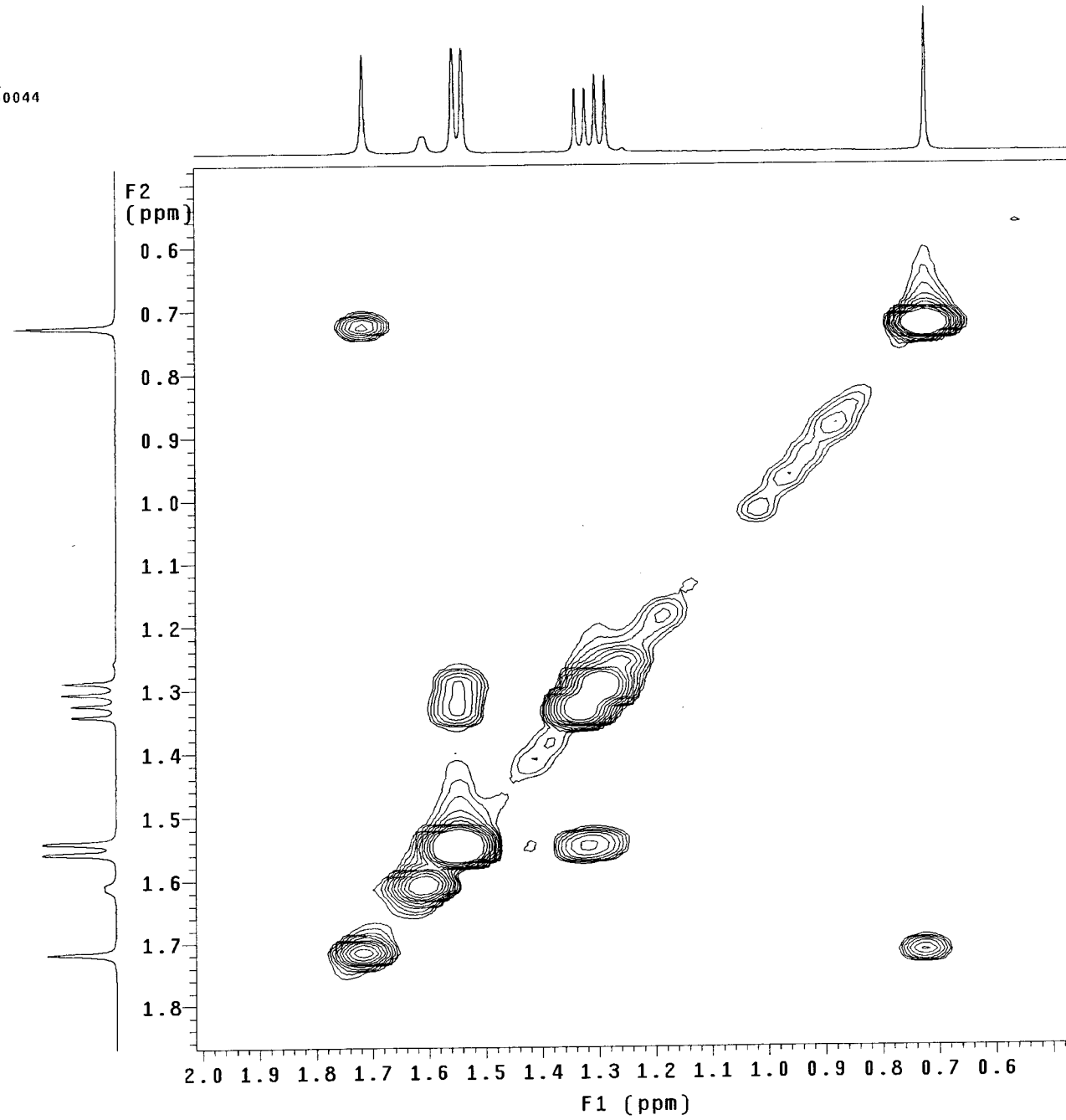
Archive directory: /export/home/robot/vnmrsys/data
Sample directory: lch-xii-115-2_loc3_2003-06-04-180044

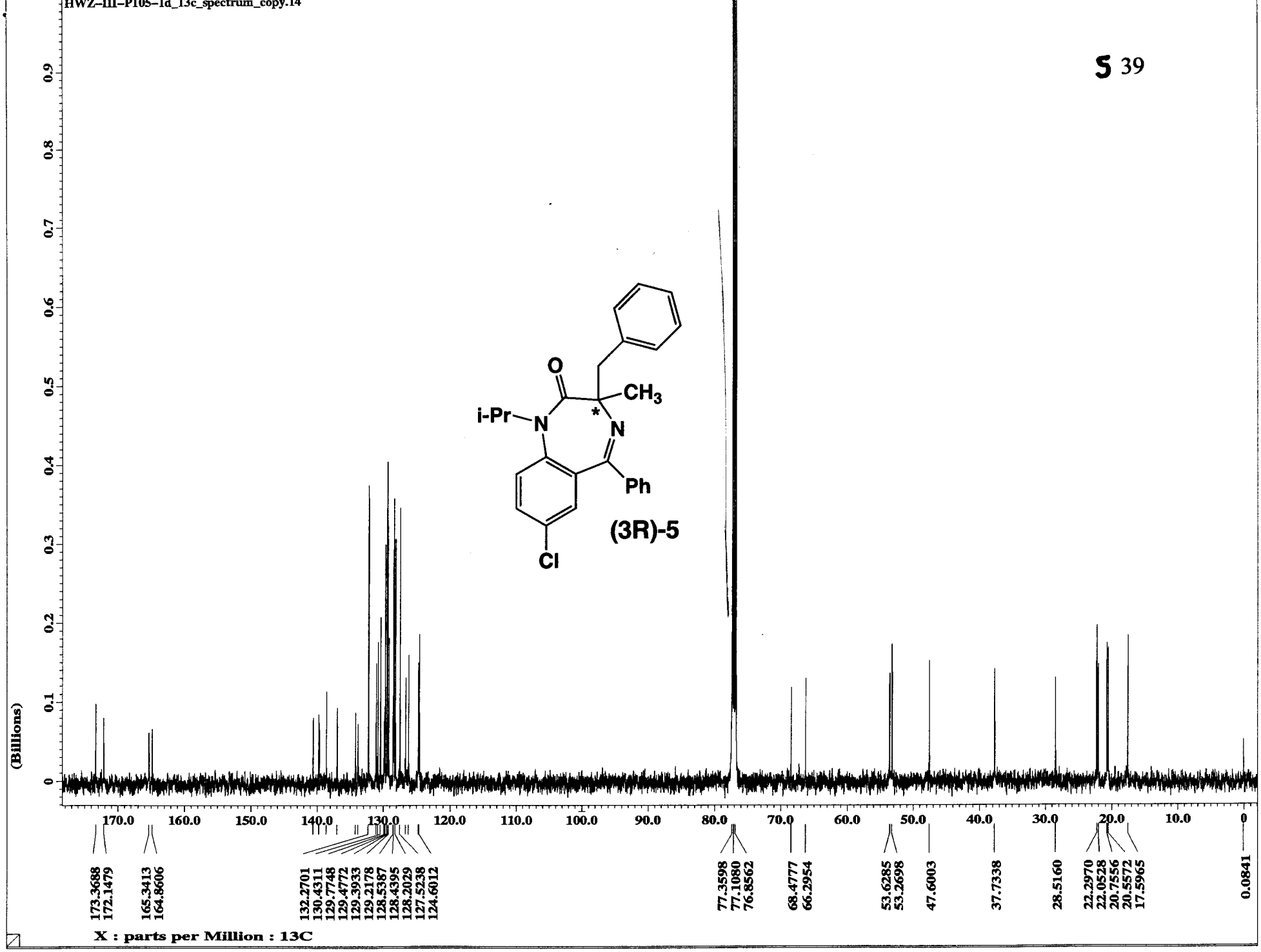
Pulse Sequence: NOESY
Solvent: CDCl3
Ambient temperature
File: NOESY_01
INOVA-400 "inova400"

Relax. delay 2.000 sec
Mixing 1.000 sec
Acq. time 0.150 sec
Width 4174.9 Hz
2D Width 4174.9 Hz
4 repetitions
2 x 128 increments
OBSERVE H1, 399.9418406 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.028 sec
FT size 2048 x 2048
Total time 55 min, 56 sec
Jun 4 2003
VA Tech Chemistry NMR Lab



(3R)-5



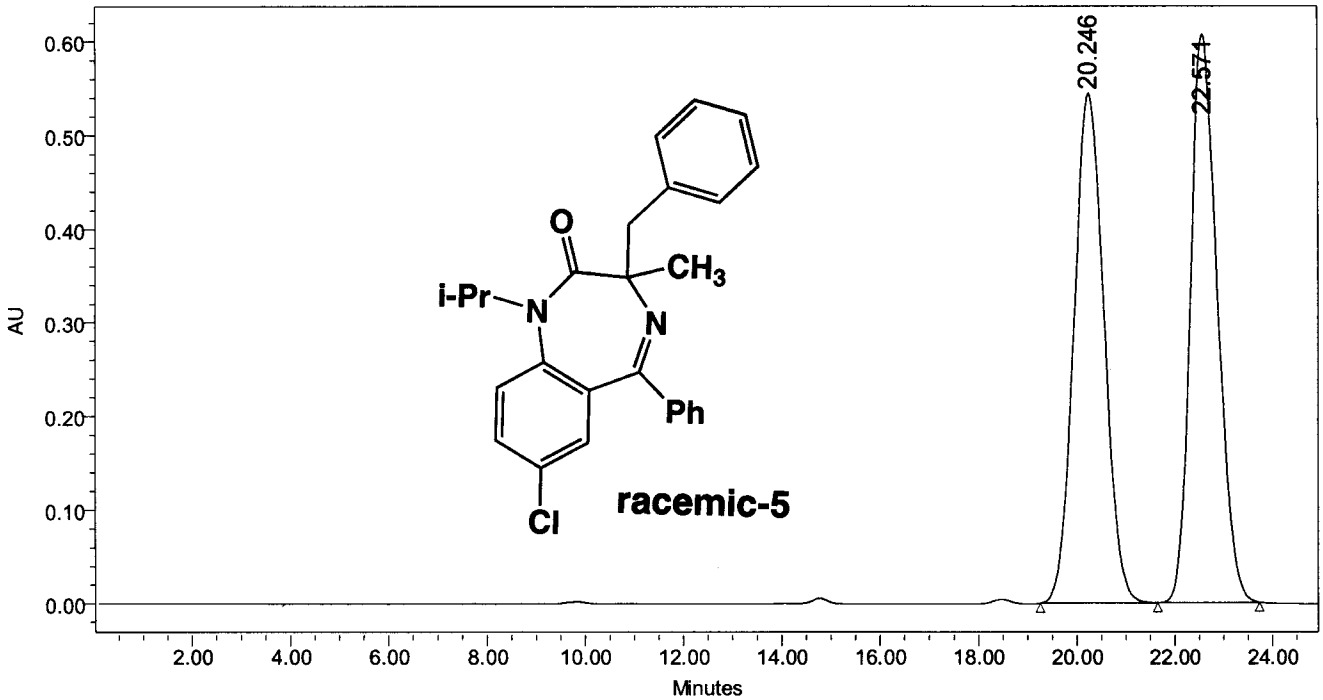

HWZ-III-P105-1d_13c_spectrum_copy.14
(Billions)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
O
CH3
i-Pr
N
*
N
Ph
Cl
(3R)-5
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.3688
172.1479
165.3413
164.8606
132.2701
130.4311
129.7748
129.4772
129.3933
129.2178
128.5387
128.4395
128.2029
127.5238
124.6012
77.3598
77.1080
76.8562
68.4777
66.2954
53.6285
53.2698
47.6003
37.7338
28.5160
22.2970
22.0528
20.7556
20.5572
17.5965
0.0841
X : parts per Million : 13C

S40

Project Name: Joe_Chiral
Reported by User: JOE

SAMPLE INFORMATION

Sample Name:	HWZ-III-53	Acquired By:	JOE
Sample Type:	Unknown	Date Acquired:	3/3/03 2:13:25 PM
Vial:	1	Acq. Method:	1% B
Injection #:	1	Date Processed:	3/3/03 4:29:55 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	JOE

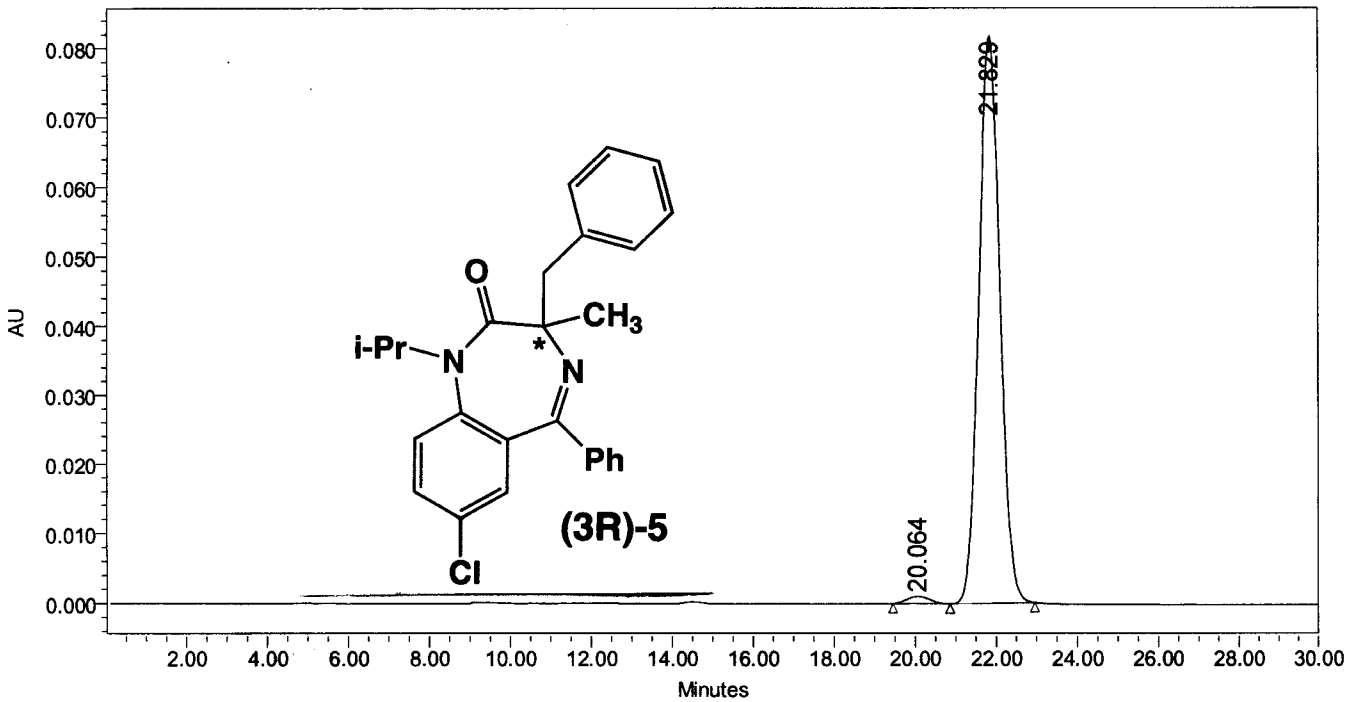


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	20.246	23102924	49.98	544191	47.29
2	22.571	23117471	50.02	606565	52.71

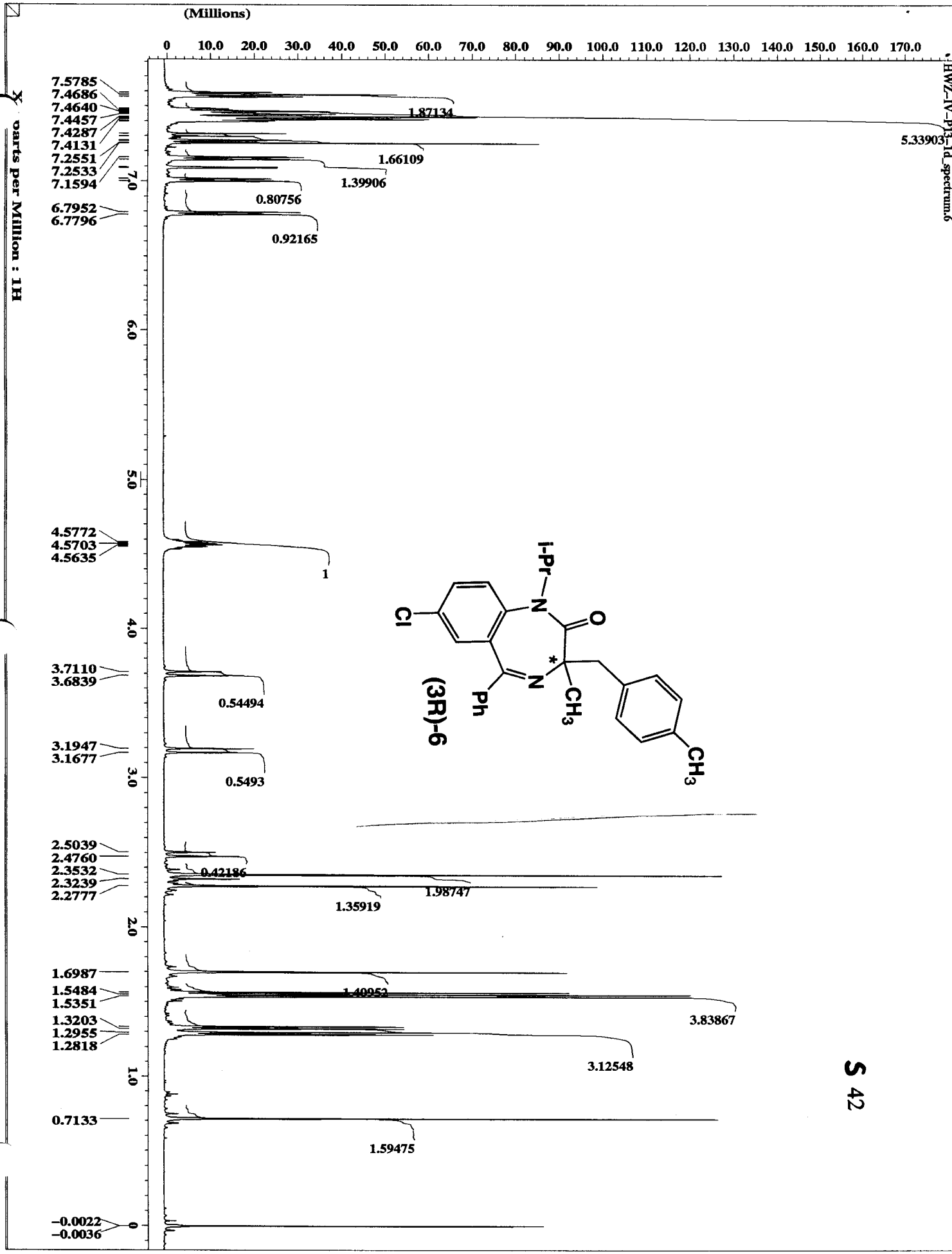
Project Name: Joe_Chiral
Reported by User: JOE

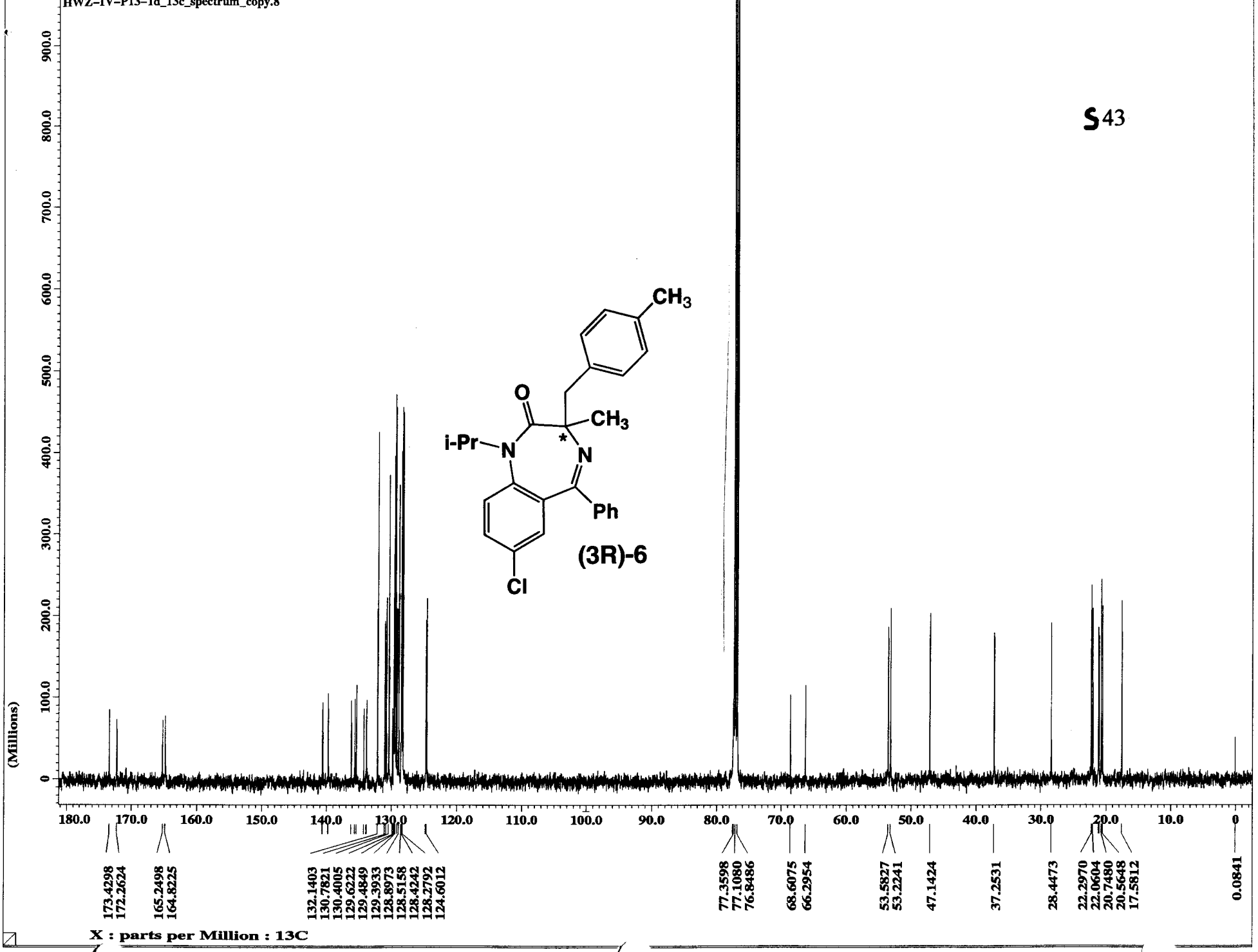
SAMPLE INFORMATION

Sample Name:	HWZ-III-P89	Acquired By:	JOE
Sample Type:	Unknown	Date Acquired:	3/3/03 6:28:46 PM
Vial:	1	Acq. Method:	1% B
Injection #:	1	Date Processed:	3/4/03 8:34:58 AM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	30.00 Minutes	Sample Set Name:	Hongwu



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	20.064	41119	1.37	1045	1.26
2	21.829	2958167	98.63	81767	98.74

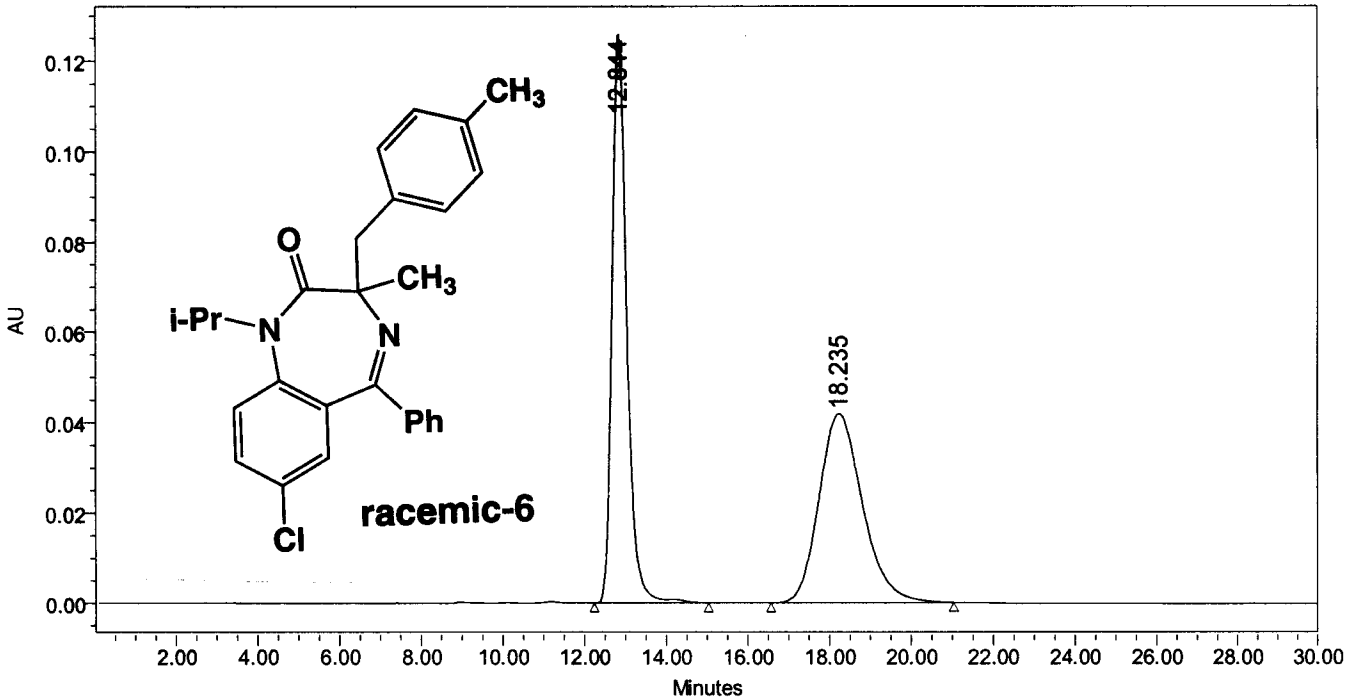

(Millions)
0 10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0 100.0 110.0 120.0 130.0 140.0 150.0 160.0 170.0
HWZ-IV-P13-1d_spectrum6
Parts per Million : 1H
7.5785
7.4686
7.4640
7.4457
7.4287
7.4131
7.2551
7.2533
7.1594
6.7952
6.7796
4.5772
4.5703
4.5635
3.7110
3.6839
3.1947
3.1677
2.5039
2.4760
2.3532
2.3239
2.2777
1.6987
1.5484
1.5351
1.3203
1.2955
1.2818
0.7133
−0.0022
−0.0036
1.87134
5.33903
1.66109
1.39906
0.80756
0.92165
1
0.54494
0.5493
0.42186
1.98747
1.35919
1.40952
3.83867
3.12548
1.59475
i-Pr
N
O
Cl
*
N
Ph
CH3
CH3
(3R)-6


HWZ-IV-P13-1d_13c_spectrum_copy.8
(Millions)
900.0
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.4298
172.2624
165.2498
164.8225
132.1403
130.7821
130.4005
129.6222
129.4849
129.3933
128.8973
128.5158
128.4242
128.2792
124.6012
77.3598
77.1080
76.8486
68.6075
66.2954
53.5827
53.2241
47.1424
37.2531
28.4473
22.2970
22.0604
20.7480
20.5648
17.5812
0.0841
X : parts per Million : 13C
CH3
O
CH3
i-Pr
N
*
N
Ph
Cl
(3R)-6

Project Name: HONGWU
Reported by User: HongWu

SAMPLE INFORMATION

Sample Name:	HWZ-IV-P13-AD-H	Acquired By:	HongWu
Sample Type:	Unknown	Date Acquired:	4/25/03 4:49:49 PM
Vial:	1	Acq. Method:	1%B
Injection #:	1	Date Processed:	4/25/03 5:20:04 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	30.00 Minutes	Sample Set Name:	Hongwu



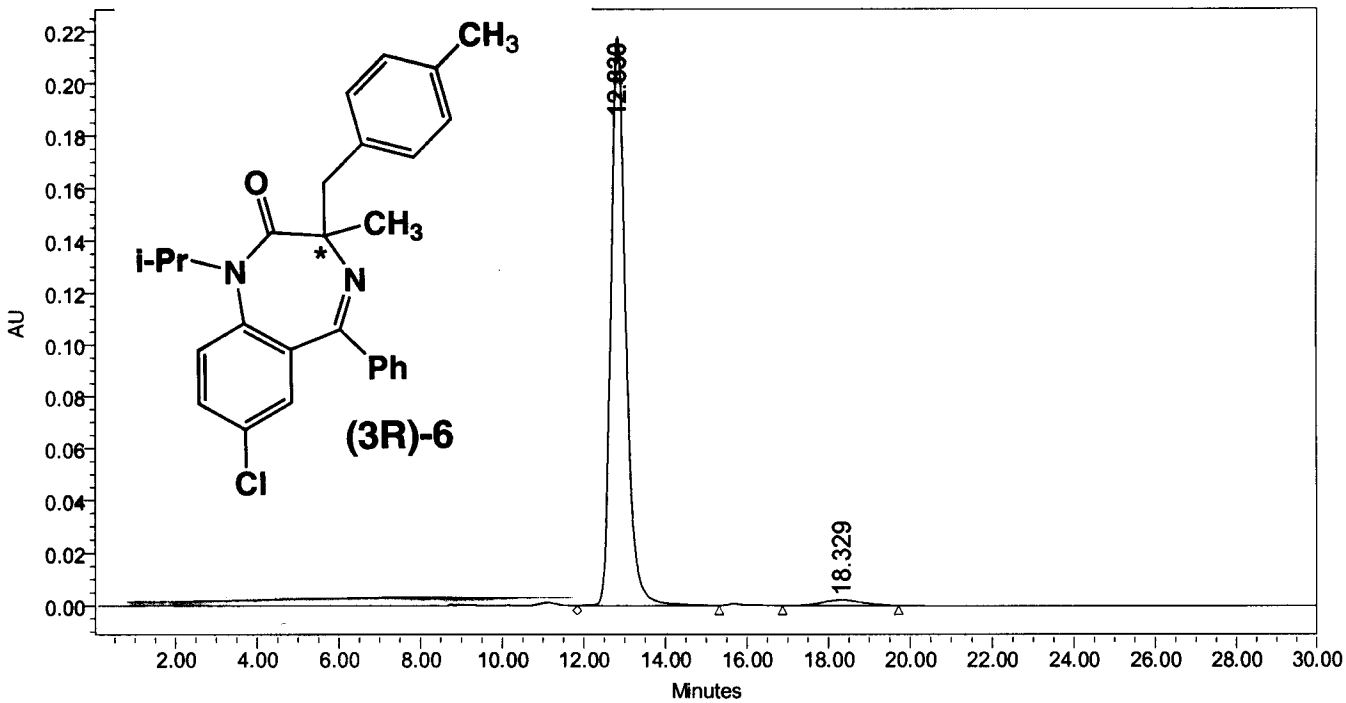
	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	12.844	3154779	50.48	125890	75.08
2	18.235	3095214	49.52	41793	24.92

S 45

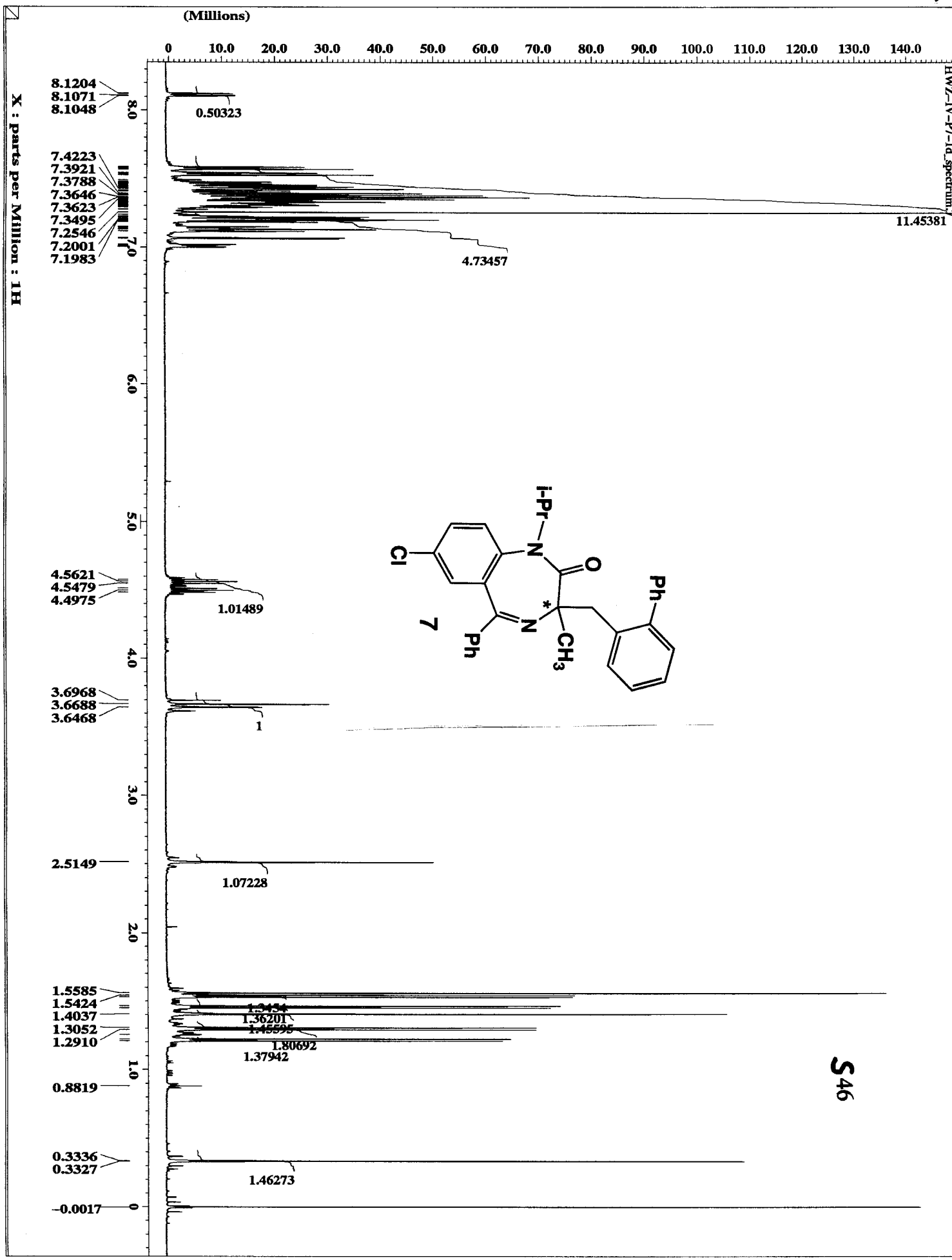
Project Name: HONGWU
Reported by User: HongWu

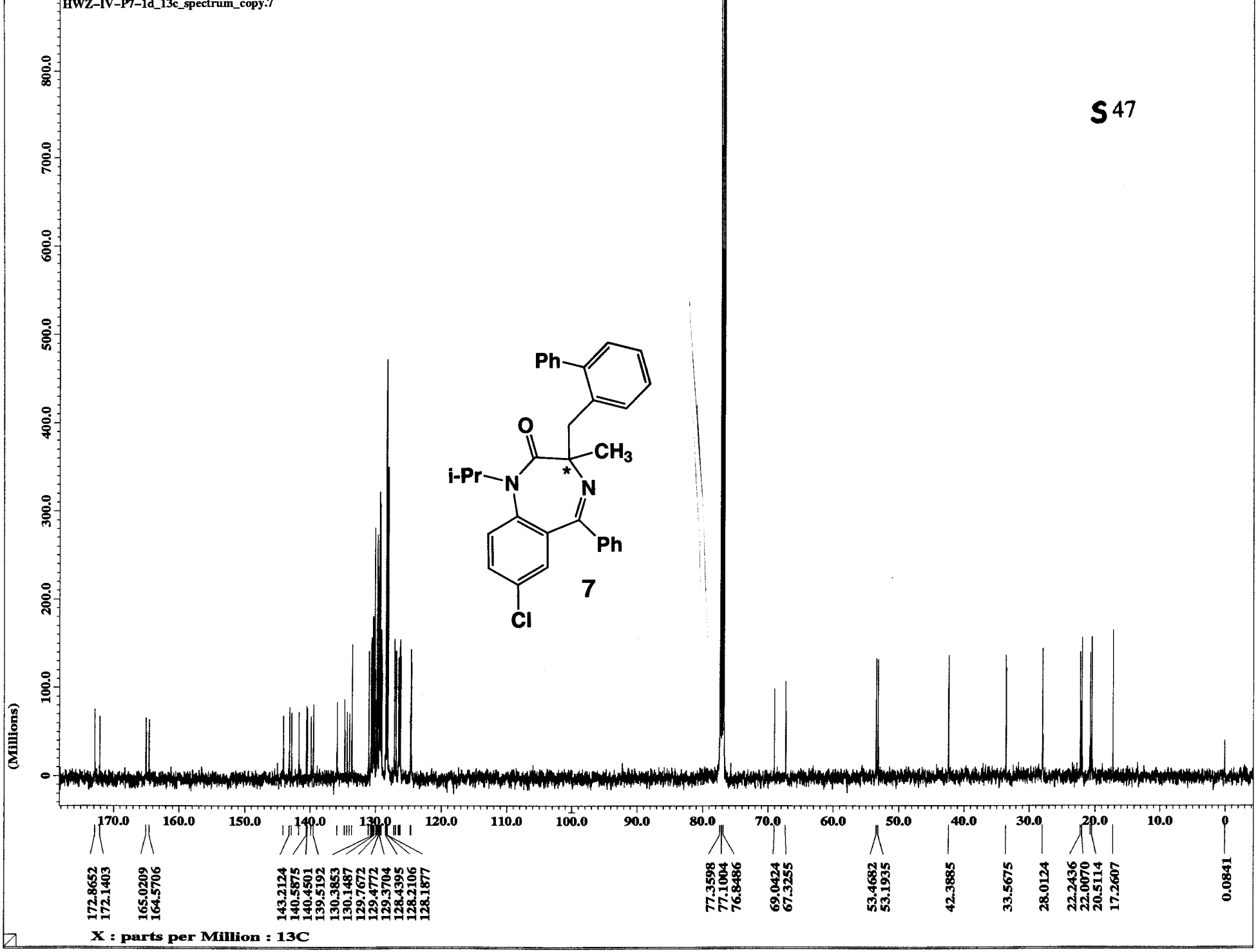
SAMPLE INFORMATION

Sample Name:	HWZ-IV-P15-AD-H	Acquired By:	HongWu
Sample Type:	Unknown	Date Acquired:	4/25/03 4:00:47 PM
Vial:	1	Acq. Method:	1%B
Injection #:	1	Date Processed:	4/25/03 4:32:16 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	30.00 Minutes	Sample Set Name:	Hongwu



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	12.830	5520068	97.59	217745	99.08
2	18.329	136467	2.41	2026	0.92


(Millions)
0 10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0 100.0 110.0 120.0 130.0 140.0
X : parts per Million : 1H
8.1204
8.1071
8.1048
0.50323
7.4223
7.3921
7.3788
7.3646
7.3623
7.3495
7.2546
7.2001
7.1983
11.45381
4.73457
4.5621
4.5479
4.4975
1.01489
3.6968
3.6688
3.6468
1
2.5149
1.07228
1.5585
1.5424
1.4037
1.3052
1.2910
1.3454
1.36201
1.45595
1.80692
1.37942
0.8819
0.3336
0.3327
1.46273
-0.0017
i-Pr
N
O
Cl
Ph
7
N
Ph
CH3
*


HWZ-IV-P7-1d_13c_spectrum_copy.7
(Millions)
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
Ph
O
CH3
i-Pr
N
*
N
Ph
7
Cl
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.8652
172.1403
165.0209
164.5706
143.2124
140.5875
140.4501
139.5192
130.3853
130.1487
129.7672
129.4772
129.3704
128.4395
128.2106
128.1877
77.3598
77.1004
76.8486
69.0424
67.3255
53.4682
53.1935
42.3885
33.5675
28.0124
22.2436
22.0070
20.5114
17.2607
0.0841
X : parts per Million : 13C

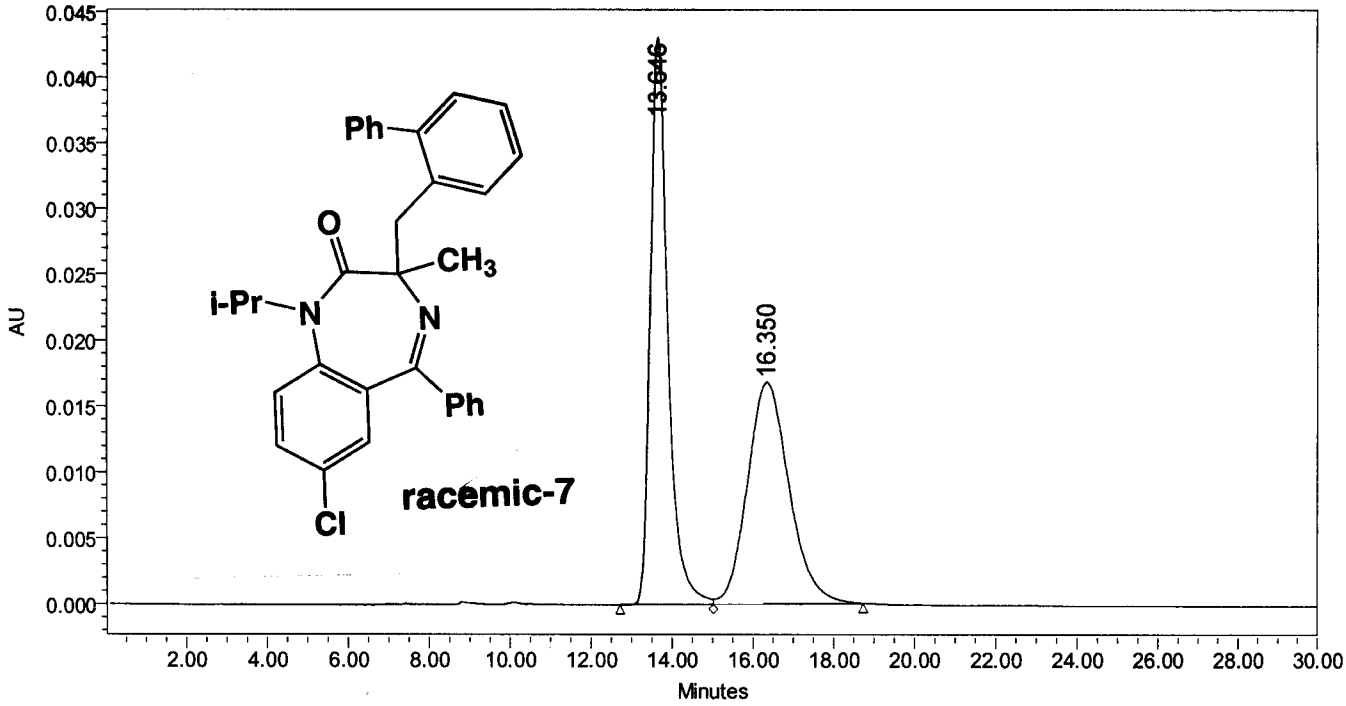
Project Name: HONGWU
Reported by User: HongWu

S48

Breeze

SAMPLE INFORMATION

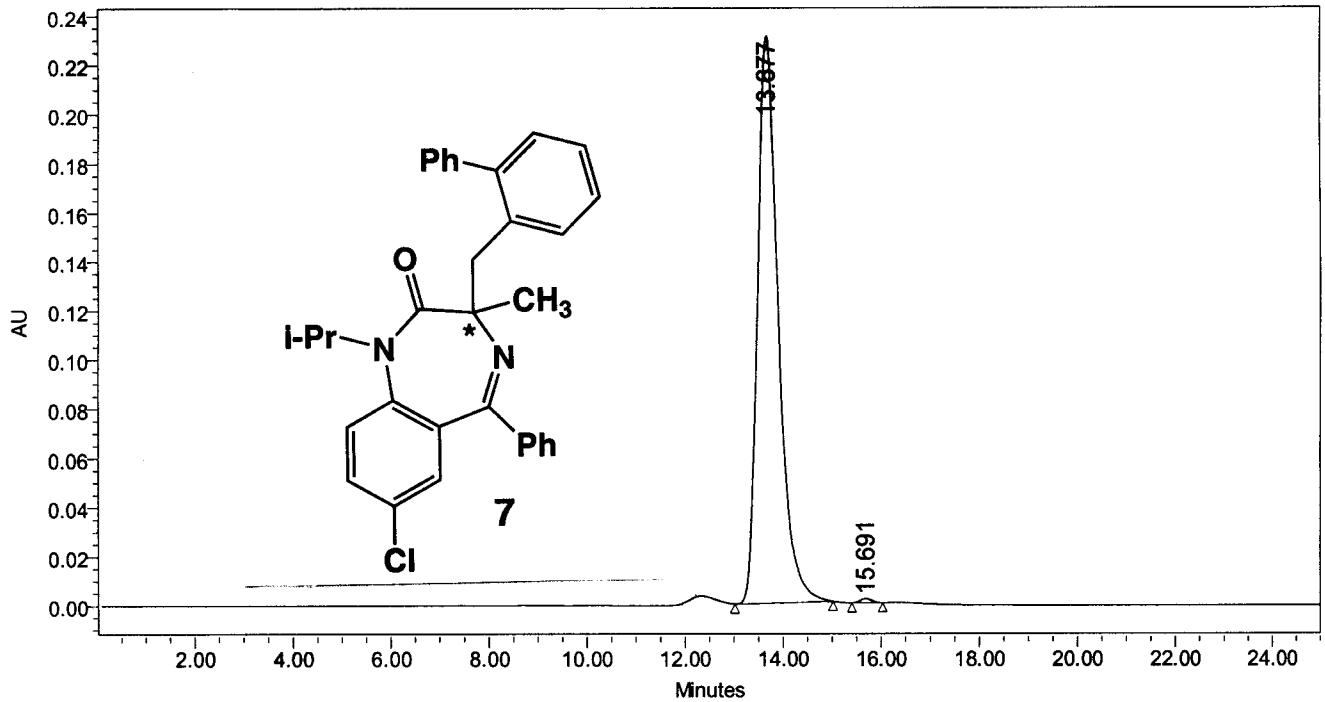
Sample Name:	HWZ-IV-P7-AD-H	Acquired By:	HongWu
Sample Type:	Unknown	Date Acquired:	4/23/03 3:21:18 PM
Vial:	1	Acq. Method:	1%B
Injection #:	1	Date Processed:	4/23/03 8:08:08 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	30.00 Minutes	Sample Set Name:	Hongwu



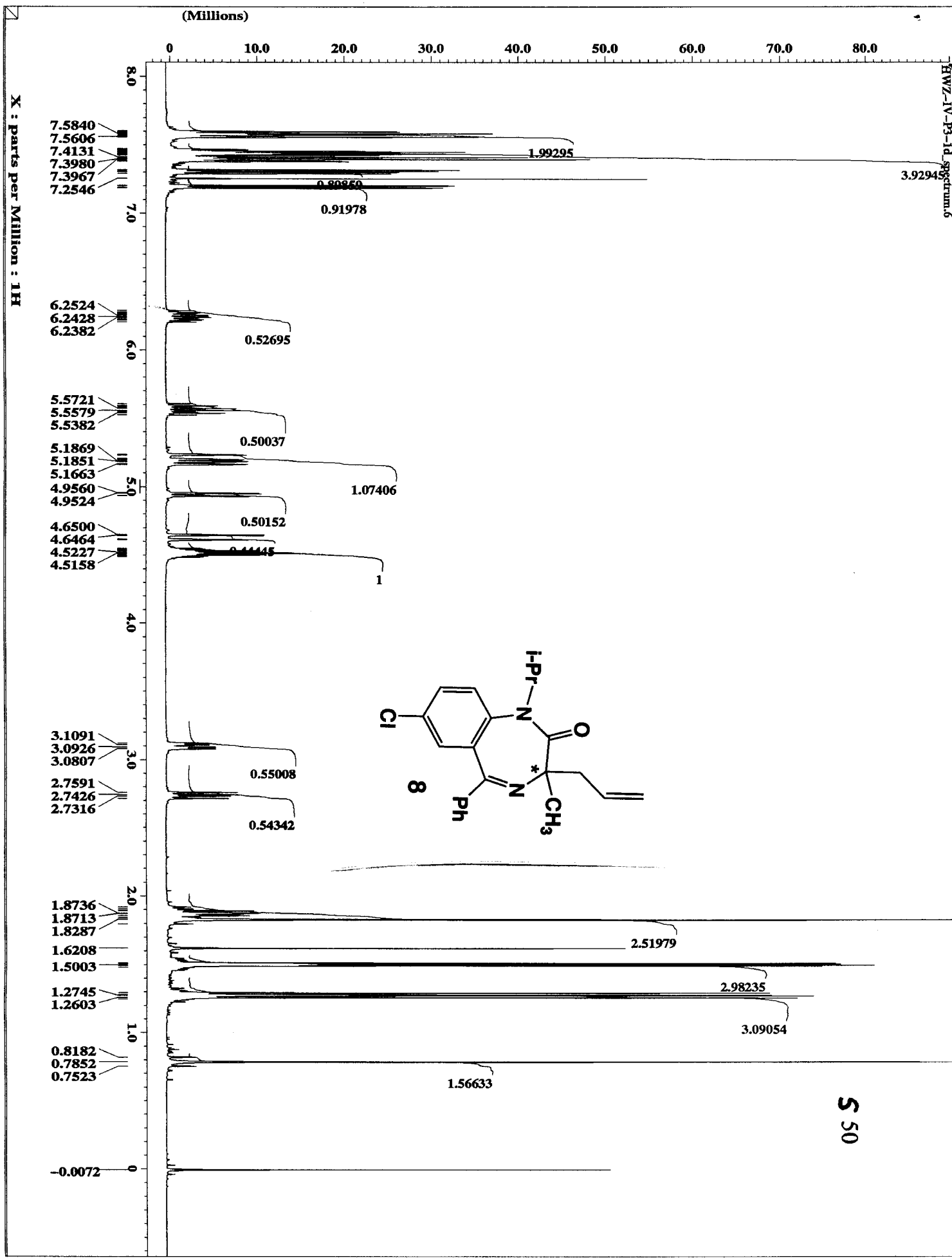
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.646	1291065	51.68	43049	71.93
2	16.350	1207204	48.32	16797	28.07

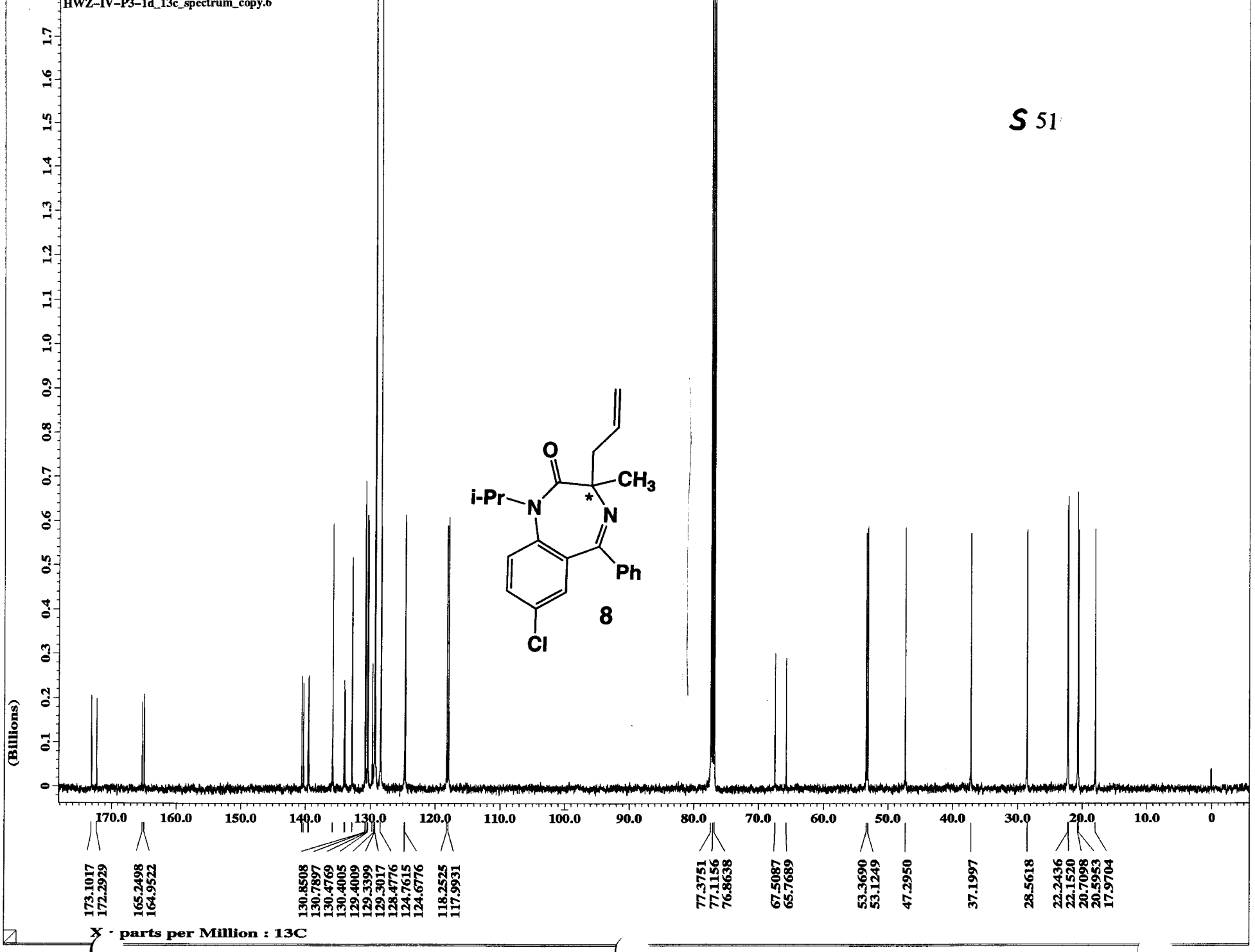
SAMPLE INFORMATION

Sample Name:	HWZ-IV-P11-AD-H	Acquired By:	HongWu
Sample Type:	Unknown	Date Acquired:	4/23/03 5:22:57 PM
Vial:	1	Acq. Method:	1%B
Injection #:	1	Date Processed:	4/23/03 6:11:50 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	25.00 Minutes	Sample Set Name:	Hongwu



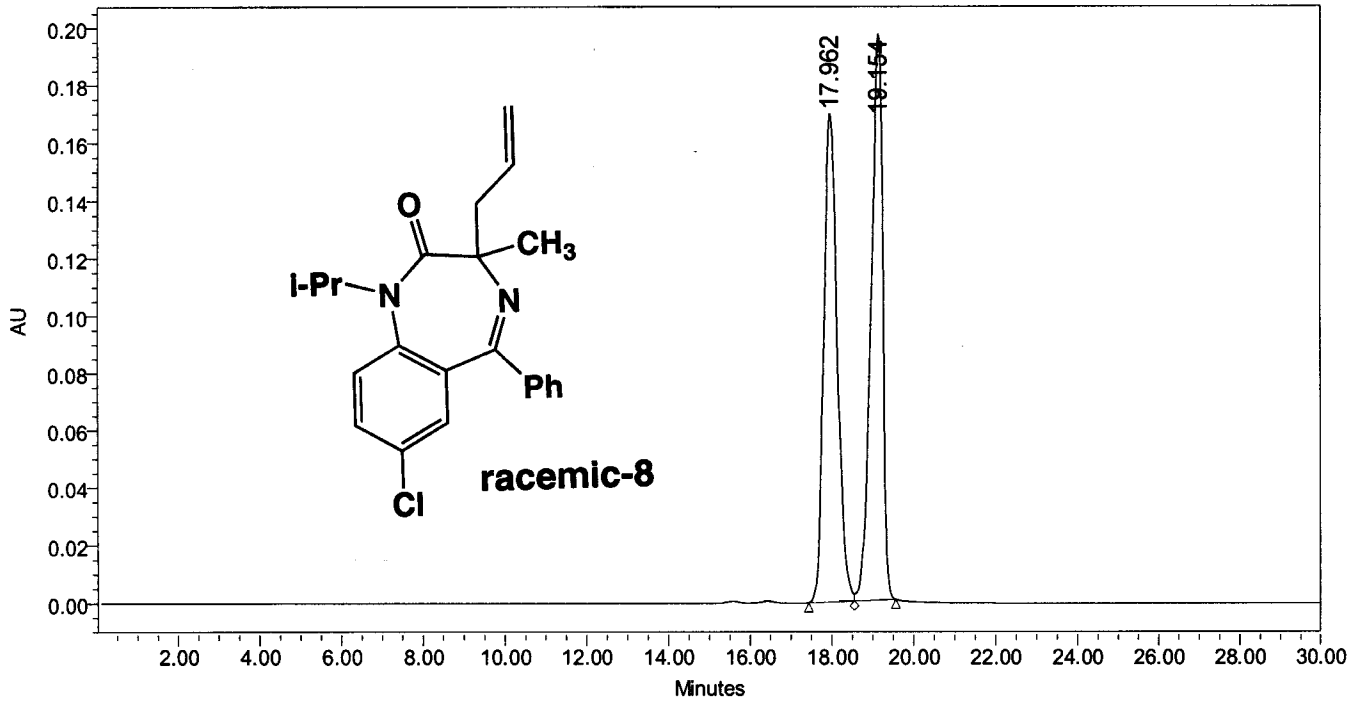
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.677	6756582	99.59	230796	99.25
2	15.691	27898	0.41	1755	0.75


(Millions)
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.5840
7.5606
7.4131
7.3980
7.3967
7.2546
6.2524
6.2428
6.2382
5.5721
5.5579
5.5382
5.1869
5.1851
5.1663
4.9560
4.9524
4.6500
4.6464
4.5227
4.5158
3.1091
3.0926
3.0807
2.7591
2.7426
2.7316
1.8736
1.8713
1.8287
1.6208
1.5003
1.2745
1.2603
0.8182
0.7852
0.7523
-0.0072
1.99295
3.92945
0.91978
0.52695
0.50037
1.07406
0.50152
1
0.55008
0.54342
2.51979
2.98235
3.09054
1.56633
i-Pr
N
O
Cl
N
*
Ph
CH3
8
HWZ-IV-P3-1d_spectrum.6
S 50


HWZ-IV-P3-1d_13c_spectrum_copy.6
(Billions)
i-Pr
N
O
CH3
*
N
Ph
Cl
8
X : parts per Million : 13C
173.1017
172.2929
165.2498
164.9522
130.8508
130.7897
130.4769
130.4005
129.4009
129.3399
129.3017
128.4776
124.7615
124.6776
118.2525
117.9931
77.3751
77.1156
76.8638
67.5087
65.7689
53.3690
53.1249
47.2950
37.1997
28.5618
22.2436
22.1520
20.7098
20.5953
17.9704

SAMPLE INFORMATION

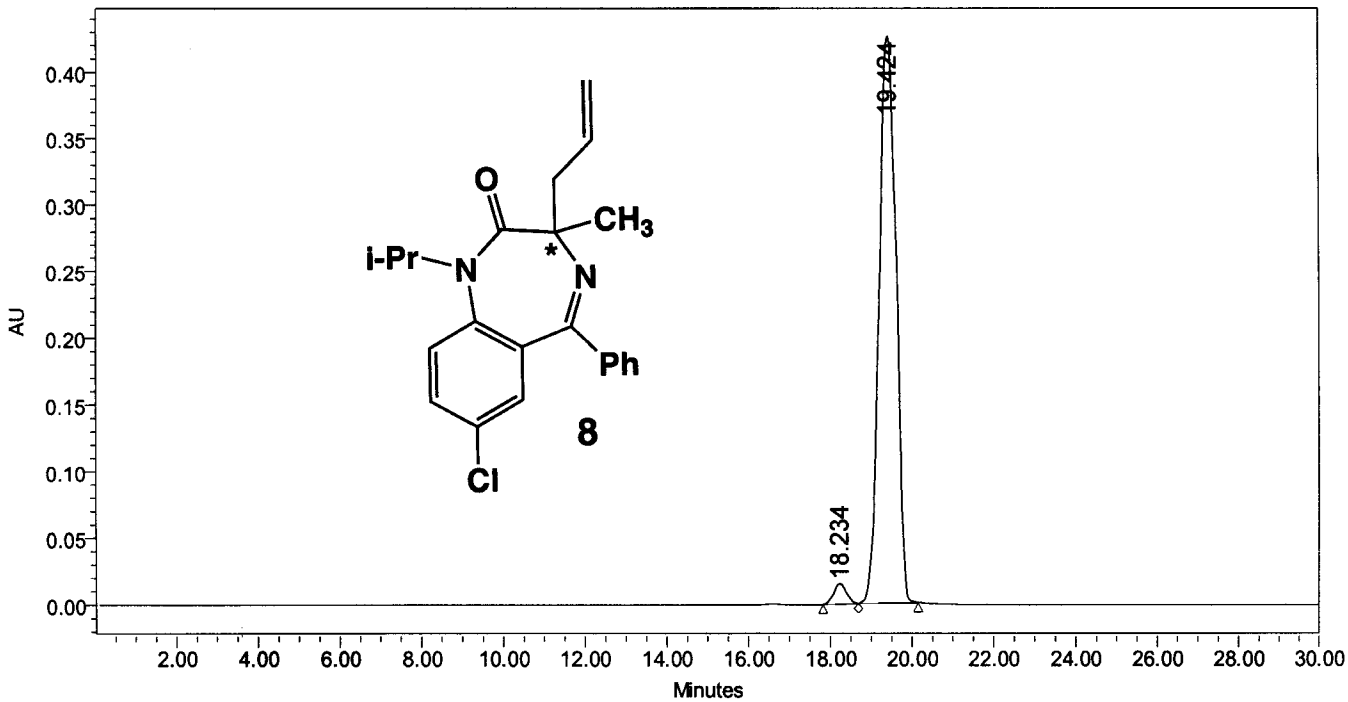
Sample Name:	HWZ-IV-P3-OD	Acquired By:	HongWu
Sample Type:	Unknown	Date Acquired:	4/17/03 6:28:37 PM
Vial:	1	Acq. Method:	0%B isopropanol
Injection #:	1	Date Processed:	4/17/03 6:58:51 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	30.00 Minutes	Sample Set Name:	Hongwu



	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	17.962	3889478	49.94	169555	46.32
2	19.154	3898105	50.06	196479	53.68

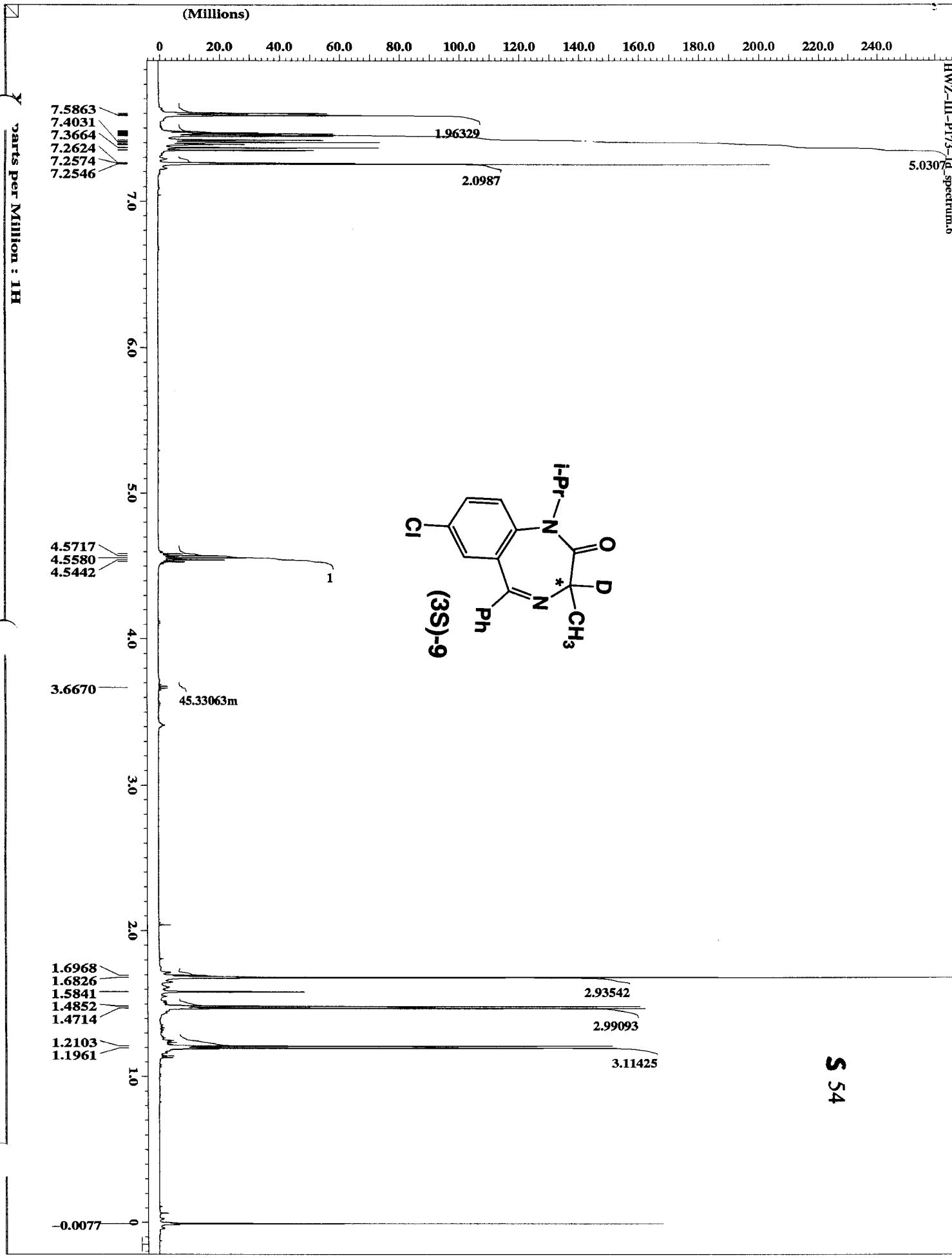
SAMPLE INFORMATION

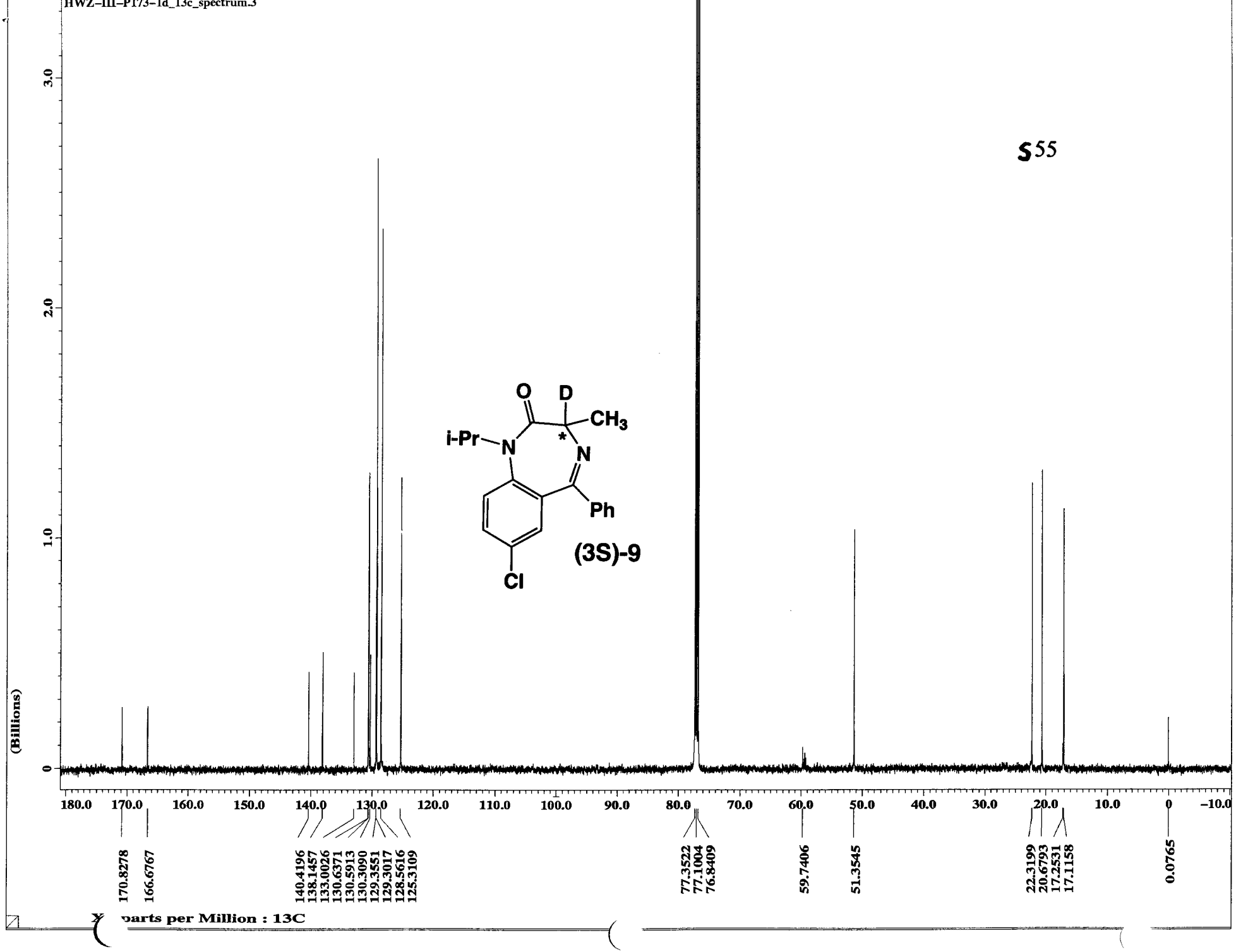
Sample Name:	HWZ-IV-P5-OD	Acquired By:	HongWu
Sample Type:	Unknown	Date Acquired:	4/17/03 7:22:17 PM
Vial:	1	Acq. Method:	0%B isopropanol
Injection #:	1	Date Processed:	4/17/03 7:52:31 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	30.00 Minutes	Sample Set Name:	Hongwu



8

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	18.234	333203	2.66	15034	3.41
2	19.424	12187607	97.34	425717	96.59

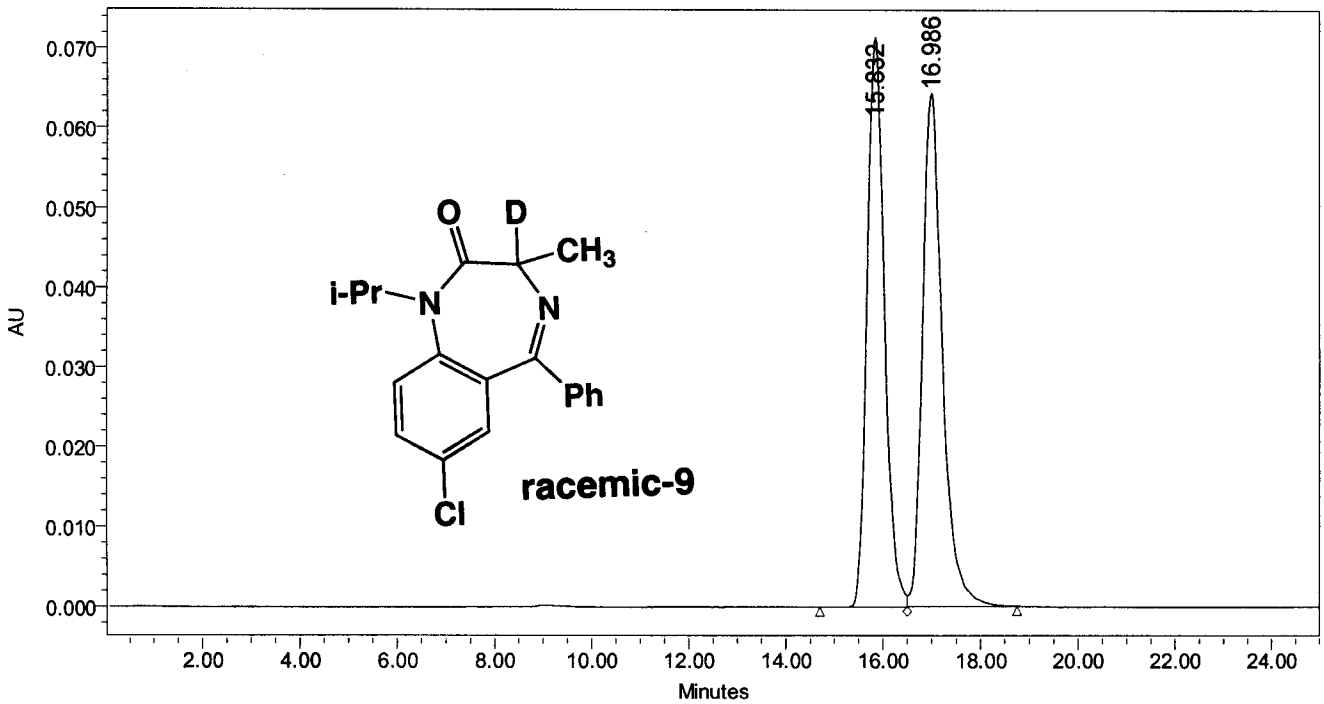

(Millions)
0 20.0 40.0 60.0 80.0 100.0 120.0 140.0 160.0 180.0 200.0 220.0 240.0
HWZ-III-P175-1d_spectrum.o
Parts per Million : 1H
7.5863
7.4031
7.3664
7.2624
7.2574
7.2546
1.96329
5.03075
2.0987
7.0
6.0
5.0
4.5717
4.5580
4.5442
1
4.0
3.6670
45.33063m
3.0
2.0
1.6968
1.6826
1.5841
1.4852
1.4714
2.93542
2.99093
1.2103
1.1961
3.11425
1.0
-0.0077
0
i-Pr
N
O
Cl
D
*
N
Ph
CH3
(3S)-9


HWZ-III-P173-1d_13c_spectrum.3
(Billions)
3.0
2.0
1.0
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
170.8278
166.6767
140.4196
138.1457
133.0026
130.6371
130.5913
130.3090
129.3551
129.3017
128.5616
125.3109
77.3522
77.1004
76.8409
59.7406
51.3545
22.3199
20.6793
17.2531
17.1158
0.0765
parts per Million : 13C
O
D
CH3
i-Pr
N
*
N
Ph
Cl
(3S)-9

Project Name: HONGWU
Reported by User: HongWu

SAMPLE INFORMATION

Sample Name:	HWZ-III-P169-AD	Acquired By:	HongWu
Sample Type:	Unknown	Date Acquired:	4/3/03 11:57:03 PM
Vial:	1	Acq. Method:	1%B
Injection #:	1	Date Processed:	5/29/03 10:02:58 AM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	25.00 Minutes	Sample Set Name:	Hognwu



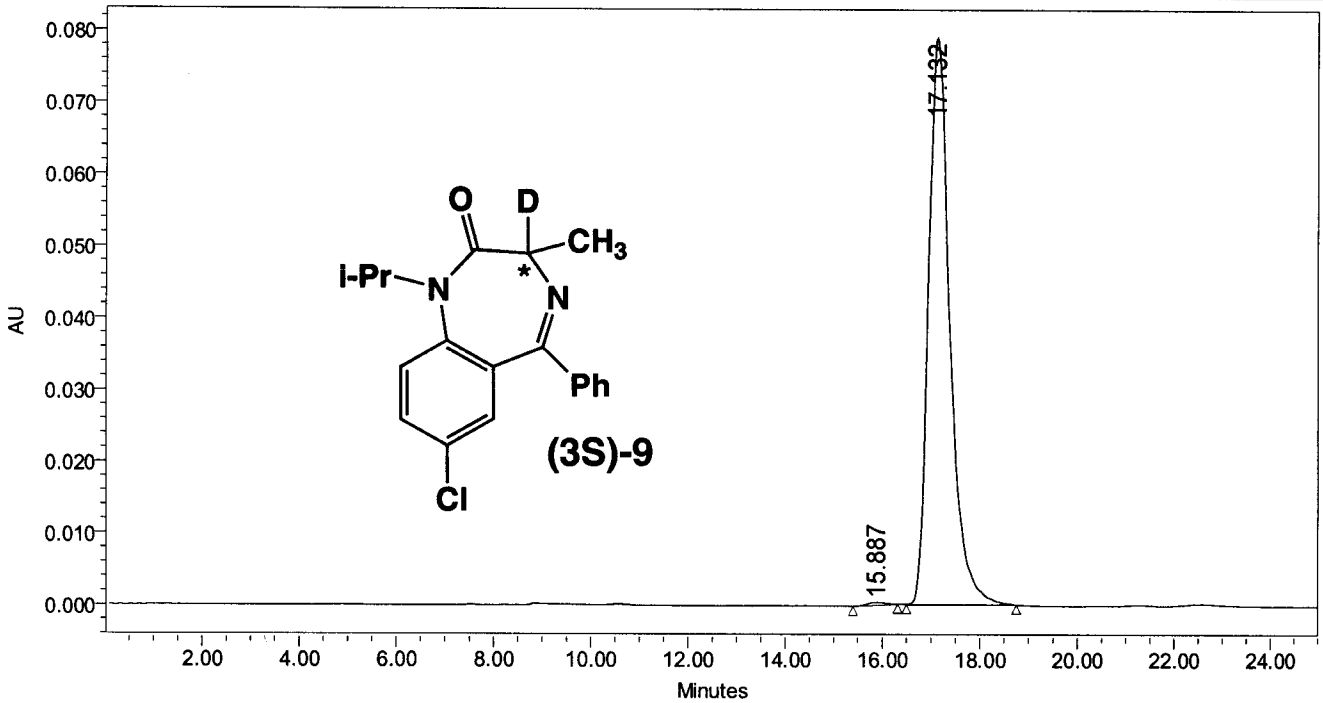
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	15.832	1770834	49.35	71374	52.58
2	16.986	1817580	50.65	64361	47.42

Project Name: HONGWU
Reported by User: HongWu

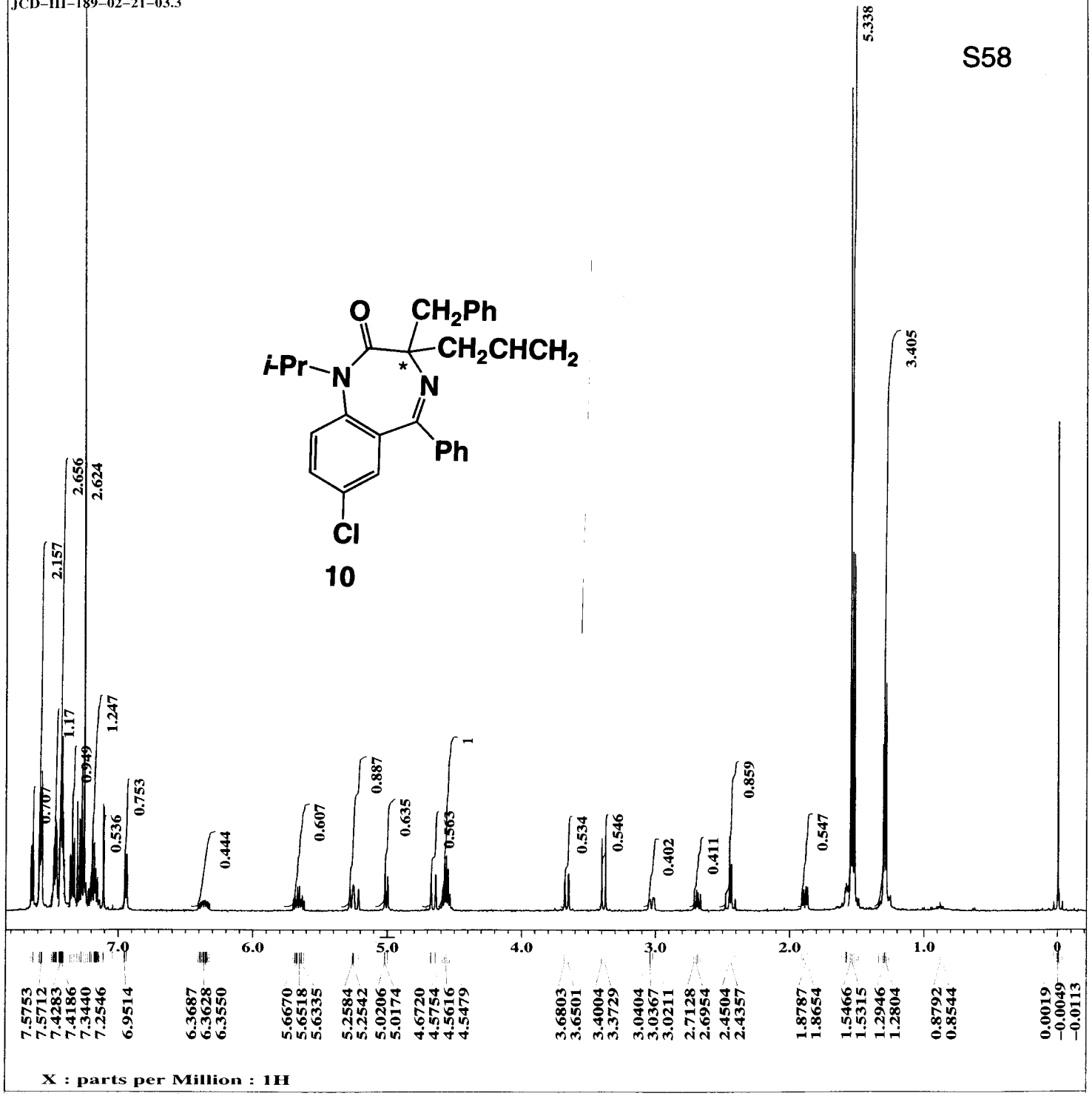
S57 Breeze

SAMPLE INFORMATION

Sample Name:	HWZ-III-P175-AD	Acquired By:	HongWu
Sample Type:	Unknown	Date Acquired:	4/3/03 10:14:39 PM
Vial:	1	Acq. Method:	1%B
Injection #:	1	Date Processed:	4/3/03 10:48:07 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	25.00 Minutes	Sample Set Name:	Hongwu



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	15.887	8982	0.37	388	0.49
2	17.132	2402732	99.63	78919	99.51



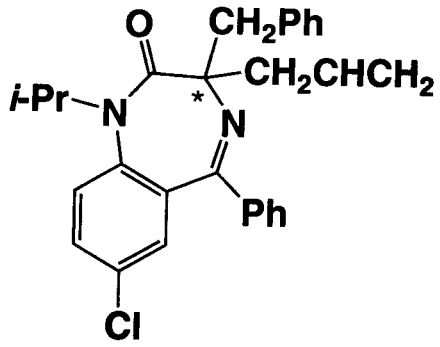

```
---- ACQUISITION PARAMETERS ----
Derived from: JCD-III-189-02-21-03.1
File Name          = JCD-III-189-02-21-03.
Author             = carlier
Sample ID          = JCD-III-189-02-21-03
Content            = Single Pulse Experime
Creation Date      = 21-MAY-2003 10:42:28

Revision Date      =  4-JUN-2003 13:15:32
Spec Site          = Eclipse+ 500

Spec Type          = DELTA_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 1H
Dim Size           = 32768
Dim Units          = [ppm]
Field_strength     = 11.7473579[T] (500[MH
X_acq_duration     = 4.3646976[s]
X_domain           = 1H
X_freq             = 500.15991521[MHz]
X_offset           = 5[ppm]
X_points           = 32768
X_prescans         = 0
X_resolution       = 0.22911095[Hz]
X_sweep            = 7.50750751[kHz]
Mod_return         = 1
Scans              = 32
Total_scans        = 32

X_90_width         = 11.5[us]
X_acq_time         = 4.3646976[s]
X_angle            = 30[deg]
X_pulse            = 3.83333333[us]
Initial_wait       = 1[s]
Phase_preset       = 3[us]
Relaxation_delay   = 1[s]
Unblank_time       = 2[us]
```

jcd-iii-177

Archive directory: /export/home/robot/vnmrsys/data
Sample directory: jcd-iii-177_loc3_2003-04-29-180043

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: CARBON_01
INOVA-400 "inova400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25141.4 Hz
5000 repetitions
OBSERVE C13, 100.5654514 MHz
DECOUPLE H1, 399.9438386 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 3 hr, 4 min, 1 sec
Apr 29 2003
VA Tech Chemistry NMR Lab



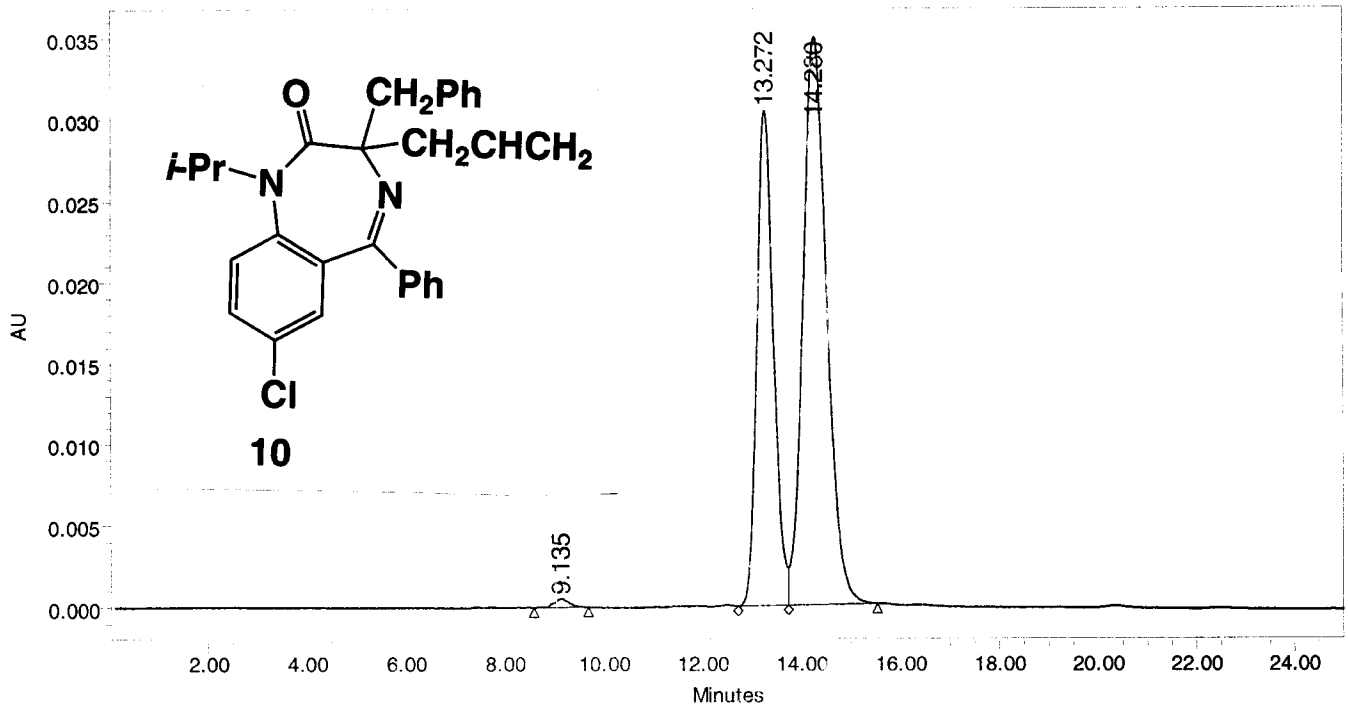
10

Project Name: Joe_Chiral
Reported by User: JOE

S60 Breeze

SAMPLE INFORMATION

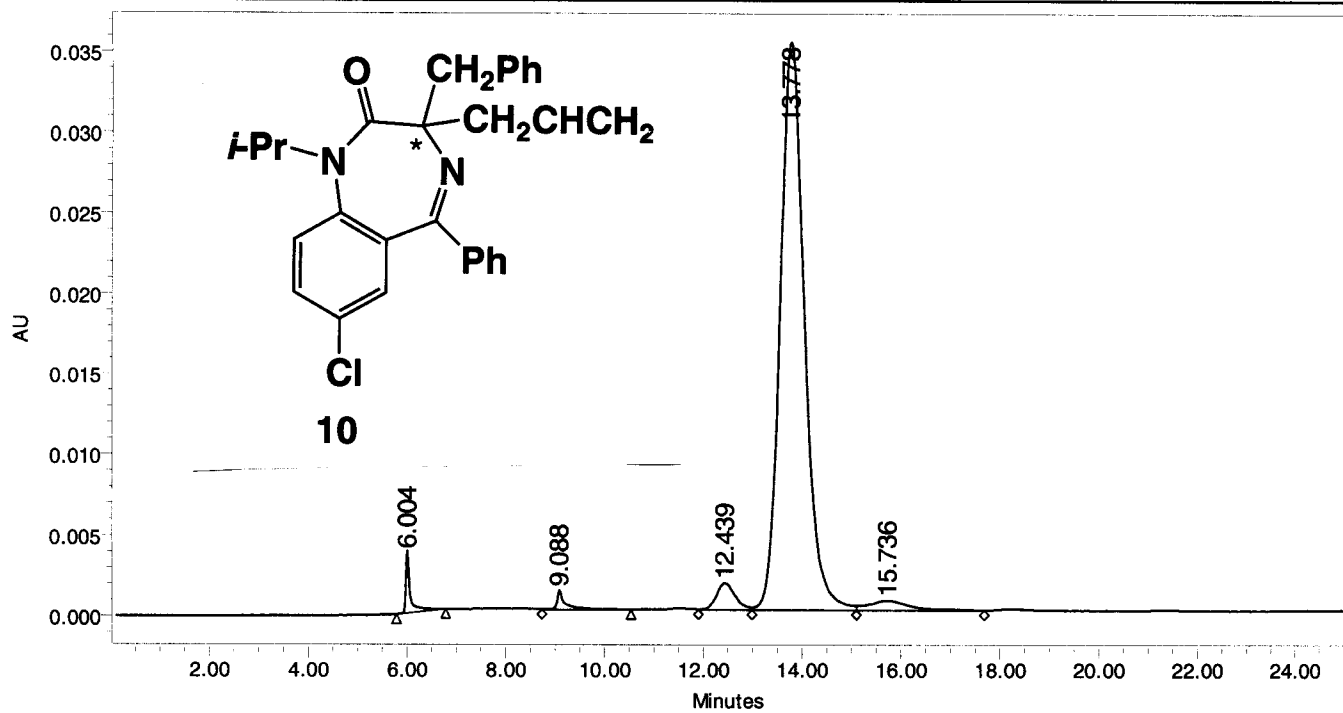
Sample Name:	JCD-III-177-III-179AD-H	Acquired By:	JOE
Sample Type:	Unknown	Date Acquired:	4/30/03 4:22:52 PM
Vial:	1	Acq. Method:	1% B
Injection #:	1	Date Processed:	4/30/03 5:37:49 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	25.00 Minutes	Sample Set Name:	JOE



	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	9.135	10899	0.58	520	0.79
2	13.272	708235	37.75	30407	46.21
3	14.280	1157119	61.67	34874	53.00

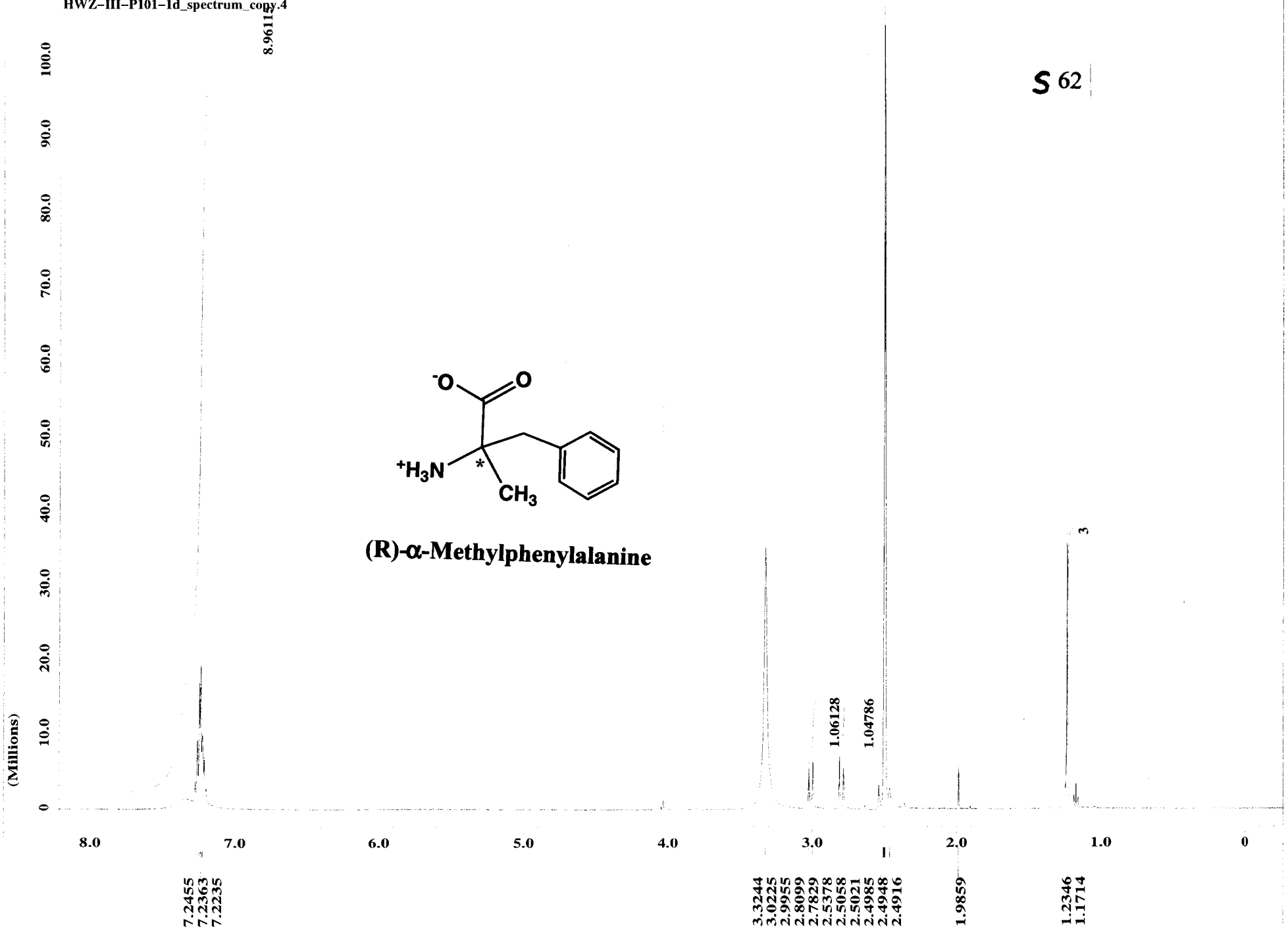
SAMPLE INFORMATION

Sample Name:	JCD-III-179AD-H	Acquired By:	JOE
Sample Type:	Unknown	Date Acquired:	4/30/03 5:21:44 PM
Vial:	2	Acq. Method:	1% B
Injection #:	1	Date Processed:	4/30/03 5:52:05 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	25.00 Minutes	Sample Set Name:	JOE



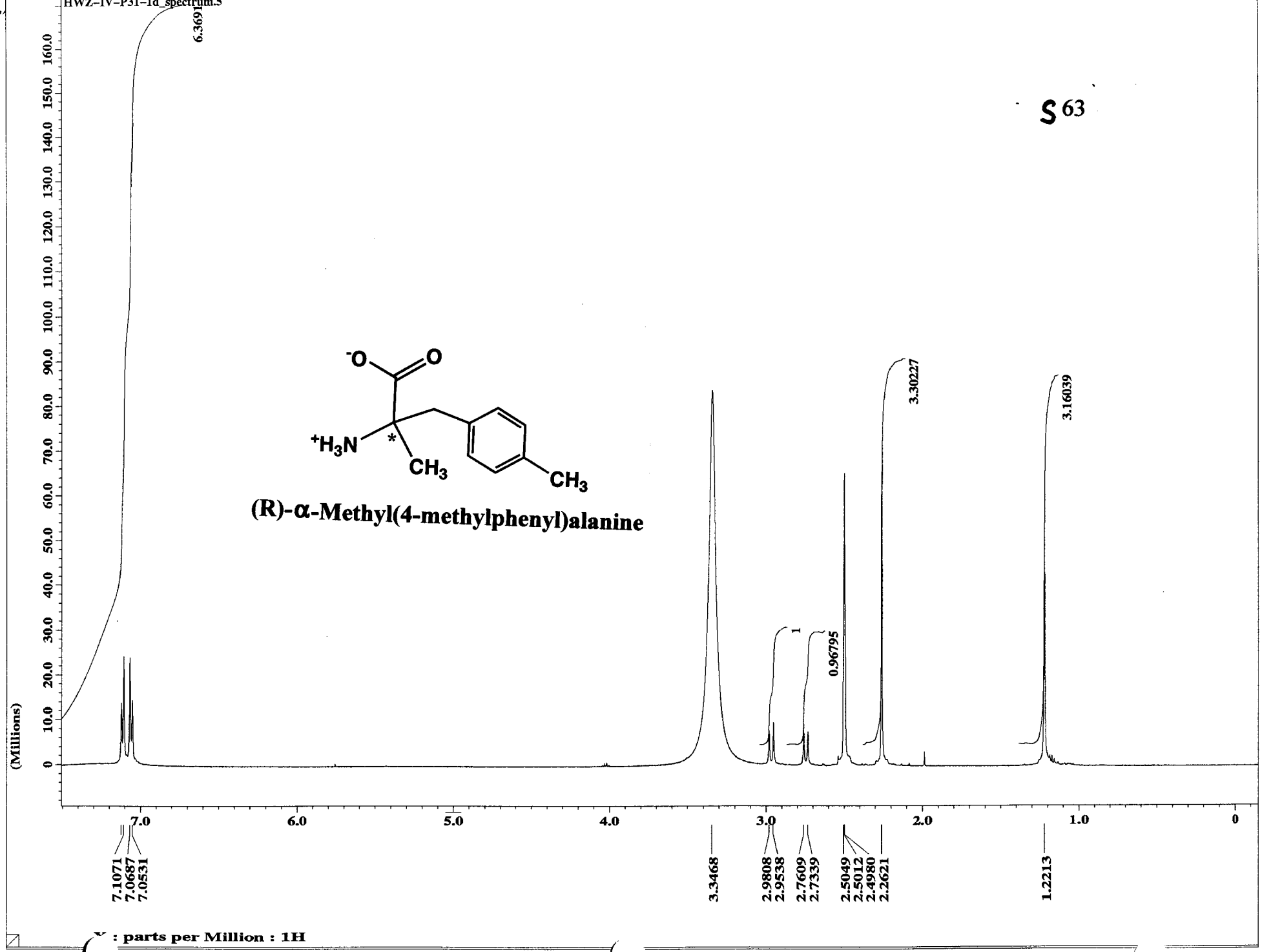
	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	6.004	24358	1.85	3767	8.87
2	9.088	14706	1.12	1173	2.76
3	12.439	43734	3.32	1657	3.90
4	13.778	1197978	91.00	35261	83.05
5	15.736	35738	2.71	598	1.41

HWZ-III-P101-1d_spectrum_copy.4

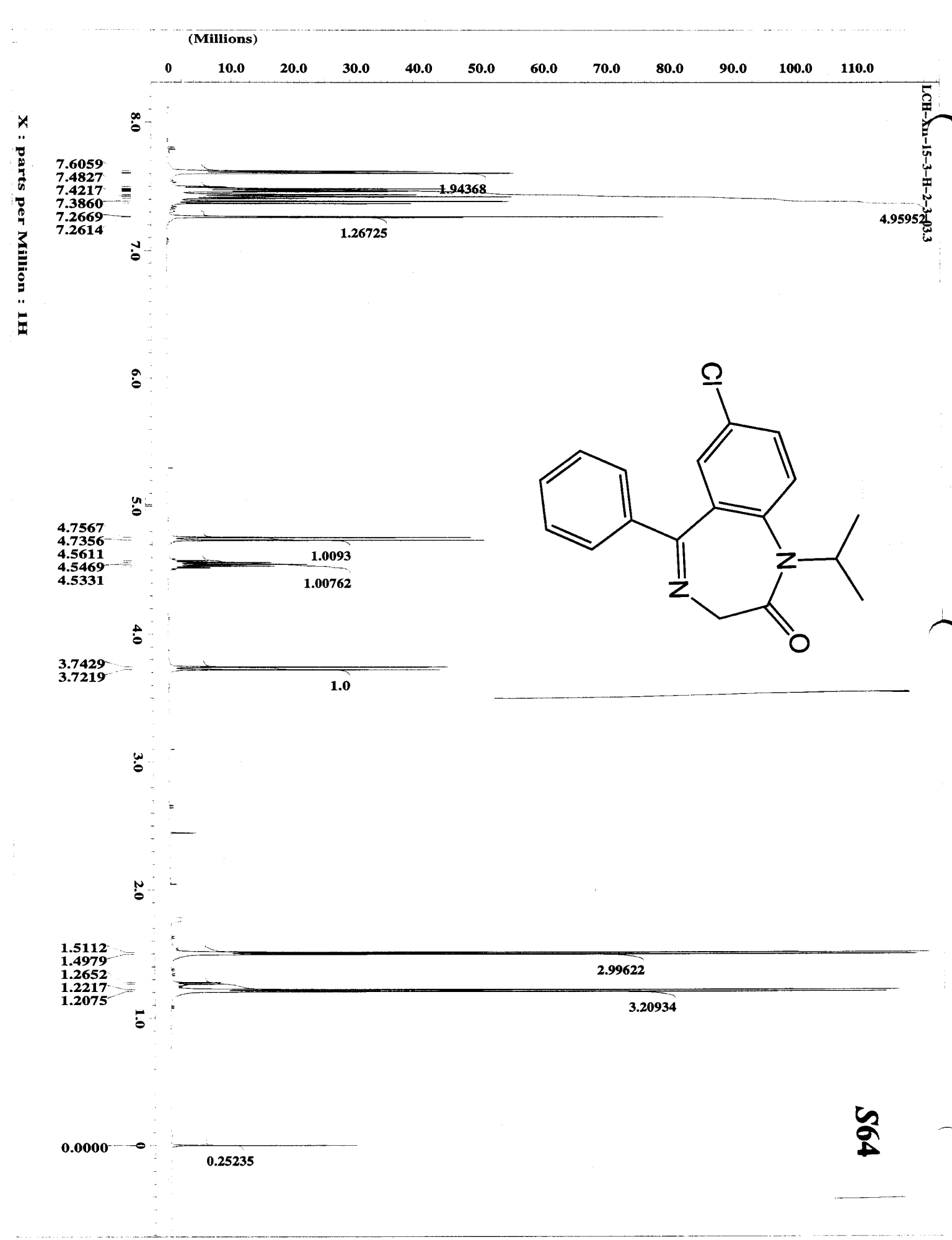


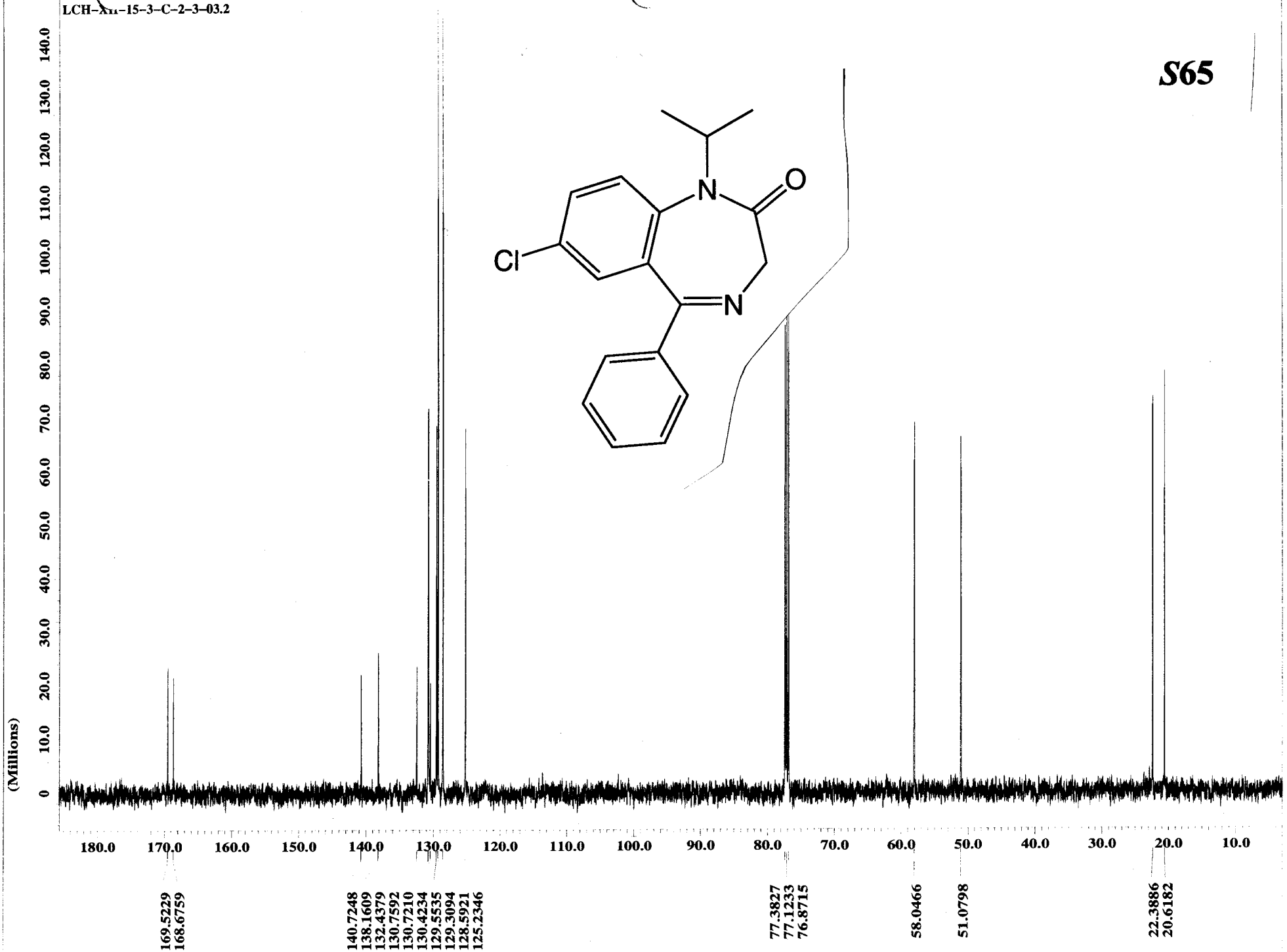
(R)-α-Methylphenylalanine

X : parts per Million : 1H



(R)-α-Methyl(4-methylphenyl)alanine


(Millions)
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
LCH-Xu-15-3-H-2-3 03.3
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.6059
7.4827
7.4217
7.3860
7.2669
7.2614
1.94368
4.95952
1.26725
4.7567
4.7356
4.5611
4.5469
4.5331
1.0093
1.00762
3.7429
3.7219
1.0
1.5112
1.4979
1.2652
1.2217
1.2075
2.99622
3.20934
0.0000
0.25235
Cl
N
N
O


LCH-XII-15-3-C-2-3-03.2
(Millions)
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
169.5229
168.6759
140.7248
138.1609
132.4379
130.7592
130.7210
130.4234
129.5535
129.3094
128.5921
125.2346
77.3827
77.1233
76.8715
58.0466
51.0798
22.3886
20.6182
X : parts per Million : 13C

N
O
Cl
N