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Supporting Information

Highly Stereoselective Iodolactonization of 4,5-Allenoic Acids-An Efficient Synthesis of 5-(1'-Iodo-1'(*Z*)-alkenyl)-4,5-dihydro-2(3*H*)-furanones

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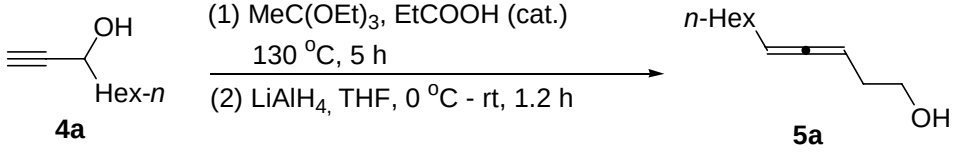
Supporting Information

Preparation of γ-allenoic acids[1] 1a-m. Typical procedure.

(1) Preparation of Dodeca-4,5-dienoic acid (1a)

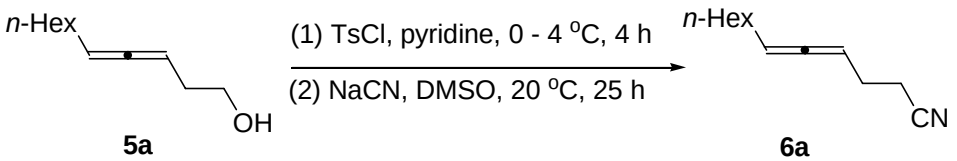
(a) Synthesis of undeca-3,4-dien-1-ol (5a)



4a **5a**

A mixture of nonyn-3-ol (**4a)** (7.0010 g, 0.05 mol), EtCOOH (1 mL, *d* = 0.99 g/mL, 0.99 g, 0.013 mol), and $MeC(OEt)_3$ (30 mL, *d* = 0.876 g/mL, 26.28 g, 0.16 mol) was heated at 130 °C for 5 h with a Dean-stark apparatus to remove the in-situ formed EtOH and the excess $MeC(OEt)_3$. After removing most of the compounds with low boiling points, the mixture was cooled to rt and then purified by chromatography on silica gel to afford ethyl undeca-3,4-dienoate (9.8926 g, crude yield 94%). The product was used in the next step without further characterization. To an ice-cold suspension of $LiAlH_4$ (1.3310 g, 34.9 mmol) in anhydrous THF (25 mL) under N_2 was dropwise added a solution of the above prepared ethyl undeca-3,4-dienoate (5.6457 g, 26.9 mmol) in THF (25 mL). After 1.2 h, the reaction was complete as monitored by TLC, quenched by slow addition of H_2O, extracted with 60 mL of ethyl ether, filtrated to remove the solid. The resulting mixture was extracted with ether and the combined organic layer was washed with water and brine, dried over Na_2SO_4, filtrated, evaporated, and purified by chromatography on silica gel to afford **5a** (3.8973 g, 86%): liquid, ^1H NMR (400 MHz, $CDCl_3$) δ 5.19-5.12 (m, 1H), 5.12-5.04 (m, 1H), 3.70 (t, *J* = 6.2 Hz, 2H), 2.28-2.21 (m, 2H), 2.02-1.95 (m, 2H), 1.64 (s, 1H), 1.43-1.21 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H). This compound was used in the next step without further characterization.

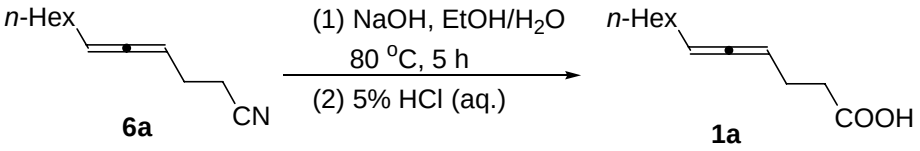
(b) Synthesis of dodeca-4,5-dienenitrile (6a)



5a **6a**

To an ice-cooled solution of **5a** (6.5161 g, 0.039 mol) in dry pyridine (50 mL) was added *p*-TsCl (22.2 g, 0.12 mol) in several portions at 0 - 4 ^{o}C with an ice water bath. After an additional 4 h, the mixture was poured into ice water and the resulting mixture was extracted with ether (50 mL × 3). The combined organic layer was washed with water and brine, dried over Na_2SO_4, filtrated, and concentrated in vacuum. The product was then used in the next step without further purification. To a mixture of tosylate prepared above and anhydrous DMSO (30 mL) was added NaCN (2.0526 g, 0.042 mol) at 20 ^{o}C. The reaction mixture was stirred for 25 h at this temperature, quenched with 30 mL of H_2O, and extracted with ether (30 mL × 3). The organic layer was washed with water and brine, dried over Na_2SO_4, filtrated, evaporated, and purified by chromatography on silica gel to afford **6a** (5.0199 g, the combined yield from **5a** to **6a** is 73%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31-5.20 (m, 1H), 5.20-5.10 (m, 1H), 2.42 (t, *J* = 7.0 Hz, 2H), 2.35-2.28 (m, 2H), 2.06-1.97 (m, 2H), 1.45-1.20 (m, 8H), 0.88 (t, *J* = 6.6 Hz, 3H). This compound was used in the next step without further characterization.

(c) Synthesis of dodeca-4,5-dienoic acid (1a)

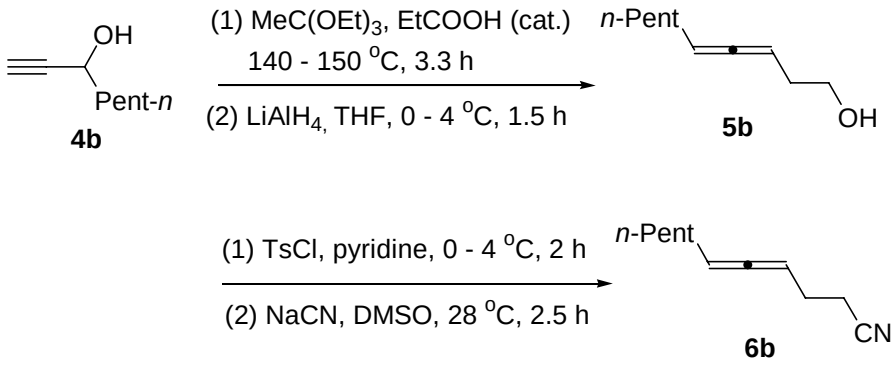


A mixture of dodeca-4,5-dienenitrile (2.0040 g, 11.3 mmol), ethanol (15 mL), and NaOH solution (4.0 g in 5.2 mL of H_2O, 100 mmol) was stirred at 80 ^{o}C for 5 h. The mixture was concentrated in vacuum and the residue was quenched with water (20 mL). The aqueous solution was then extracted with ether to remove neutral impurities. The aqueous layer was then acidified with 5% HCl (aq.) to pH = 1 and extracted with ether (30 mL × 3). The ether extraction was washed with water and brine, dried over Na_2SO_4, filtrated, and concentrated in vacuum. Chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) of the crude product afforded **1a** (2.1065 g, 95%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.82 (bs, COOH, 1H), 5.21-5.09 (m, 2H), 2.48 (t, *J* = 7.1 Hz, 2H), 2.36-2.23 (m, 2H), 2.03-1.90 (m, 2H), 1.46-1.16 (m, 8H), 0.88 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 179.6, 92.9, 89.2, 33.1, 31.7, 29.1, 28.84, 28.82,

23.5, 22.6, 14.1; IR (neat) ν = 3030, 2957, 2927, 2856, 1964, 1712, 1435, 1336, 1278, 1211, 1173 cm^{-1}; MS (70 ev, EI) *m/z* (%) 196 (M^+, 0.46), 126 (100); HRMS Calcd for $C_{12}H_{20}O_2Na$ (M^++Na): 219.1356, Found: 219.1351.

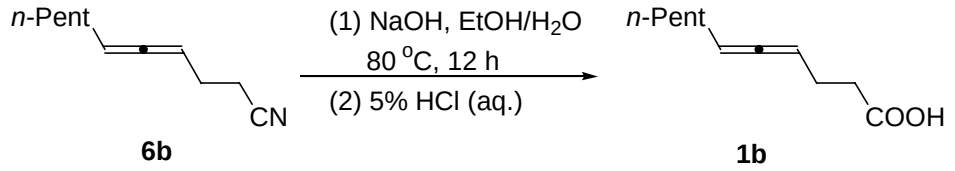
(2) Preparation of undeca-4,5-dienoic acid (1b)

(a) Synthesis of undeca-4,5-dienenitrile (6b)



Following the procedure for the preparation of **5a**, the reaction of octyn-3-ol (**4b**) (7.5609 g, 0.060 mol), EtCOOH (1.5 mL, *d* = 0.99 g/mL, 1.49 g, 0.020 mol), and $MeC(OEt)_3$ (36 mL, 0.876 g/mL, 0.19 mol, 31.54 g) afforded ethyl deca-3,4-dienoate (7.9972 g). The product was used in the next step without further characterization. A solution of this ester (7.9972 g, 0.041 mol) in anhydrous THF (20 mL) was treated with $LiAlH_4$ (1.8573 g, 0.049 mol) in anhydrous THF (30 mL) to afford **5b** (5.9947 g). The product was used in the next step without further characterization. Following the procedure for the preparation of **6a**, the reaction of **5b** (3.0065 g, 0.018 mol), *p*-TsCl (6.8239 g, 0.036 mol), and anhydrous pyridine (30 mL) afforded the tosylate, which was used in the next step without further purification. The reaction of tosylate prepared above and NaCN (0.9454 g, 0.019 mmol) in anhydrous DMSO (30 mL) afforded **6b** (2.0203 g, the combined yield from **4b** to **6b** is 41%): liquid, ^1H NMR (300 MHz, $CDCl_3$) δ 5.32-5.21 (m, 1H), 5.21-5.11 (m, 1H), 2.47-2.39 (m, 2H), 2.37-2.27 (m, 2H), 2.07-1.96 (m, 2H), 1.47-1.22 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H). This compound was used in the next step without further characterization.

(b) Synthesis of undeca-4,5-dienoic acid (1b)

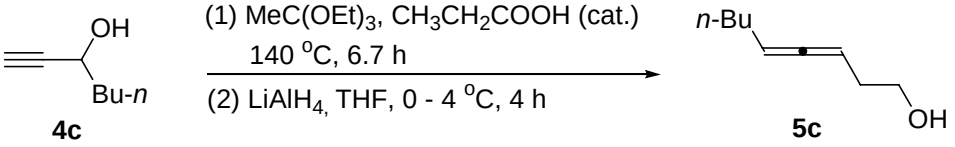


6b **1b**

Following the procedure for the preparation of **1a**, the reaction of undeca-4,5-dienenitrile (1.0112 g, 6.2 mmol), ethanol (15 mL), and NaOH solution (4.0 g in 5 mL of H_2O, 100 mmol) afforded **1b**[1] (0.8485 g, 75%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.08 (bs, COOH, 1H), 5.22-5.10 (m, 2H), 2.48 (t, *J* = 7.1 Hz, 2H), 2.37-2.18 (m, 2H), 2.05-1.88 (m, 2H), 1.48-1.20 (m, 6H), 0.88 (t, *J* = 6.3 Hz, 3H). This compound was used in the next step without further characterization.

(3) Preparation of deca-4,5-dienoic acid (1c)

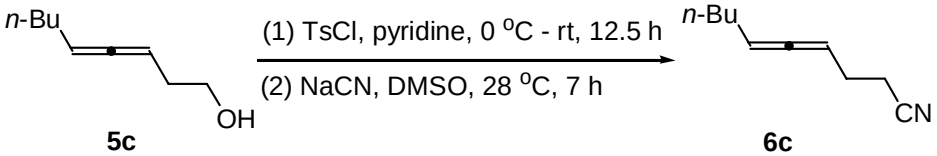
(a) Synthesis of nona-3,4-dien-1-ol (5c)



4c **5c**

Following the procedure for the preparation of **5a**, the reaction of heptyn-3-ol (**4c**) (5.6276 g, 0.05 mol), EtCOOH (1.5 mL, *d* = 0.99 g/mL, 1.49 g, 0.020 mol), and $MeC(OEt)_3$ (28 mL, *d* = 0.876 g/mL, 24.53 g, 0.15 mol) afforded ethyl nona-3,4-dienoate (8.7706 g, crude yield 96%). The product was used in the next step without further characterization. A solution of ester (8.6174 g, 0.048 mol) in anhydrous THF (10 mL) was treated with $LiAlH_4$ (1.8184 g, 0.048 mol) in anhydrous THF (50 mL) to afford **5c** (6.1902 g, 93%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.18-5.11 (m, 1H), 5.11-5.04 (m, 1H), 3.69 (t, *J* = 6.2 Hz, 2H), 2.28-2.21 (m, 2H), 2.04-1.95 (m, 2H), 1.73 (s, 1H), 1.44-1.27 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). This compound was used in the next step without further characterization.

(b) Synthesis of deca-4,5-dienenitrile (6c)

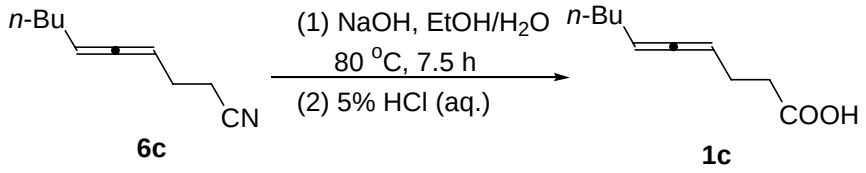


5c **6c**

Following the procedure for the preparation of **6a**, the reaction of **5c** (6.1902 g, 0.044 mol), *p*-TsCl (25.3 g, 0.13 mol), and anhydrous pyridine (30 mL) afforded the

tosylate, which was used in the next step without further purification. The reaction of tosylate prepared above and NaCN (2.3054 g, 0.047 mol) in anhydrous DMSO (40 mL) afforded **6c** (3.1615 g, the combined yield from **5c** to **6c** is 48%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31-5.21 (m, 1H), 5.19-5.11 (m, 1H), 2.45-2.39 (m, 2H), 2.37-2.26 (m, 2H), 2.07-1.96 (m, 2H), 1.46-1.28 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H). This compound was used in the next step without further characterization.

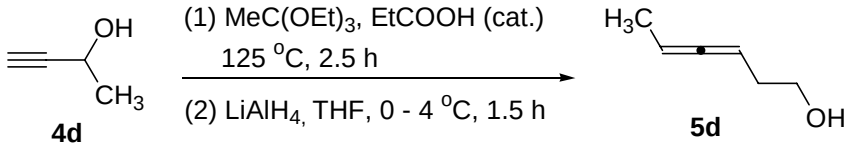
(c) Synthesis of deca-4,5-dienoic acid (1c)

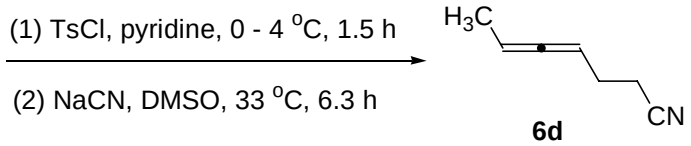


Following the procedure for the preparation of **1a**, the reaction of deca-4,5-dienenitrile (1.0054 g, 6.7 mmol), ethanol (15 mL), and aqueous NaOH solution (4.0 g in 5.2 mL of H_2O, 100 mmol) afforded **1c** (0.8769 g, 77%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.82 (bs, COOH, 1H), 5.20-5.11 (m, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.38-2.22 (m, 2H), 2.02-1.92 (m, 2H), 1.42-1.22 (m, 4H), 0.89 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.7, 179.5, 92.8, 89.2, 33.1, 31.2, 28.5, 23.5, 22.2, 13.9; IR (neat) ν = 3036, 2959, 2928, 2873, 1963, 1712, 1412, 1273, 1211 cm^{-1}; MS (70 ev, EI) *m/z* (%) 168 (M^+, 0.53), 126 (M^+-C_2H_2O, 100)[2]; HRMS Calcd for $C_{10}H_{16}O_2$ (M^+): 168.1145, Found: 168.1149.

(4) Preparation of hepta-4,5-dienoic acid (1d)

(a) Synthesis of hepta-4,5-dienenitrile (6d)

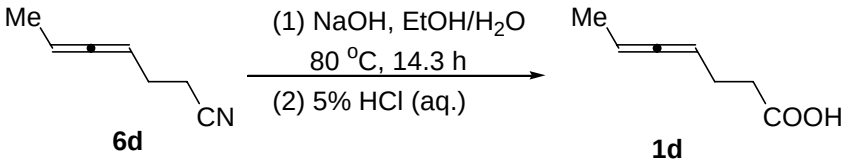




But-3-yn-2-ol (**4d**) (7.5 g, 0.11 mol) was added dropwise to the mixture of EtCOOH (1.6 mL, *d* = 0.99 g/mL, 1.58 g, 0.021 mol) and $MeC(OEt)_3$ (48.0 g, 0.30

mol) at 125 °C for 0.5 h. After being stirred for an extra 2.5 h at 125 °C, the mixture was cooled to rt, evaporated, and purified by chromatography on silica gel (2 times) to afford ethyl hexa-3,4-dienoate (8.4558 g). The product was used in the next step without further characterization. Following the procedure for the preparation of **5a**, a solution of ester (8.4558 g, 0.060 mol) in anhydrous THF (10 mL) was treated with $LiAlH_4$ (2.5337 g, 0.066 mol) in anhydrous THF (50 mL) to afford **5d** (3.9285 g, crude yield 37%). The product was used in the next step without further characterization. Following the procedure for the preparation of **6a**, the reaction of **5d** (2.0439 g, 0.02 mol), *p*-TsCl (7.78 g, 0.04 mol), and anhydrous pyridine (30 mL) afforded the tosylate, which was used in the next step without further purification. The reaction of tosylate prepared above and NaCN (0.9505 g, 0.019 mmol) in anhydrous DMSO (30 mL) afforded **6d** (1.0989 g, crude yield 49%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.30-5.18 (m, 1H), 5.18-5.08 (m, 1H), 2.47-2.40 (m, 2H), 2.35-2.26 (m, 2H), 1.69 (dd, J_1 = 6.9 Hz, J_2 = 3.3 Hz, 3H). This compound was used in the next step without further characterization.

(b) Synthesis of hepta-4,5-dienoic acid (1d)

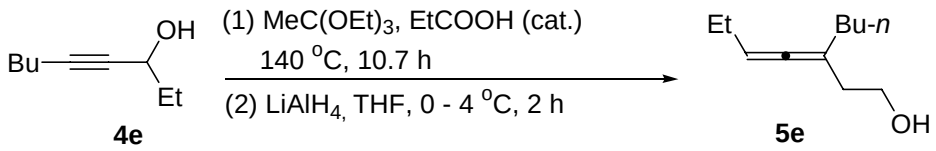


6d **1d**

Following the procedure for the preparation of **1a**, the reaction of hepta-4,5-dienenitrile (1.0124 g, 9.5 mmol), ethanol (15 mL), and NaOH solution (4.0 g in 5.2 mL of H_2O, 100 mmol) afforded **1d** (0.9340 g, 78%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.66 (bs, COOH, 1H), 5.18-5.08 (m, 2H), 2.47 (t, J = 6.8 Hz, 2H), 2.36-2.20 (m, 2H), 1.63 (t, J = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.6, 179.8, 88.7, 87.4, 33.1, 23.4, 14.3; IR (neat) ν = 3095, 3037, 2985, 2926, 1966, 1712, 1413, 1272, 1250, 1212, 1172 cm^{-1}; MS (70 ev, EI) *m/z* (%) 126 (M^+, 5.81), 84 (M^+-C_2H_2O, 100)[2]; HRMS Calcd for $C_7H_{10}O_2$ (M^+): 126.0675, Found: 126.0681.

(5) Preparation of 4-butylocta-4,5-dienoic acid (1e)

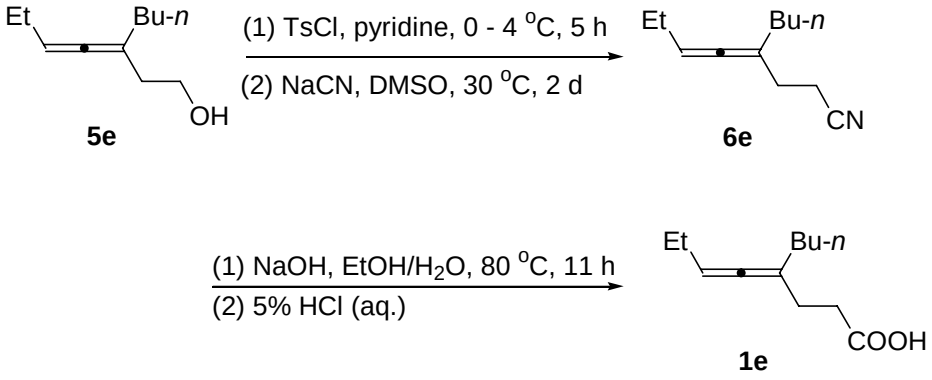
(a) Synthesis of 3-butylhepta-3,4-dien-1-ol (5e)



4e **5e**

Following the procedure for the preparation of **5a**, the reaction of dec-4-yn-3-ol (**4e**) (7.0480 g, 0.050 mol), EtCOOH (1.5 mL, *d* = 0.99 g/mL, 1.49 g, 0.020 mol), and $MeC(OEt)_3$ (28 mL, *d* = 0.876 g/mL, 24.53 g, 0.15 mol) afforded ethyl 3-butylhepta-3,4-dienoate (7.4334 g). The product was used in the next step without further characterization. A solution of ester (7.4334 g, 0.035 mol) in anhydrous THF (10 mL) was treated with $LiAlH_4$ (1.4813 g, 0.039 mol) in anhydrous THF (40 mL) to afford **5e** (1.6984 g, the combined yield from **4e** to **5e** is 20%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.26-5.19 (m, 1H), 3.71 (t, *J* = 6.0 Hz, 2H), 2.23-2.16 (m, 2H), 2.05-1.90 (m, 4H), 1.78 (s, 1H), 1.45-1.24 (m, 4H), 0.99 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). This compound was used in the next step without further characterization.

(b) Synthesis of 4-butylocta-4,5-dienoic acid (1e)



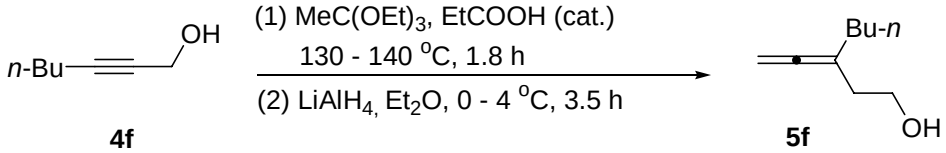
5e **6e** **1e**

Following the procedure for the preparation of **6a**, the reaction of **5e** (0.9085 g, 0.0054 mol), *p*-TsCl (3.0950 g, 0.016 mol), and anhydrous pyridine (20 mL) afforded the tosylate, which was used in the next step without further purification. The reaction of tosylate prepared above and NaCN (0.2878 g, 0.0058 mmol) in anhydrous DMSO (20 mL) afforded **6e** (0.6733 g). The product was used in the next step without further characterization. Following the procedure for the preparation of **1a**, the reaction of 4-butylocta-4,5-dienenitrile (0.6733 g, 3.8 mmol), ethanol (10 mL), and NaOH solution (2 g in 2.5 mL of H_2O, 50 mmol) afforded **1e** (0.4871 g, the combined yield from **5e** to **1e** is 46%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.62 (bs, COOH, 1H),

5.28-5.14 (m, 1H), 2.48 (t, J = 7.2 Hz, 2H), 2.34-2.12 (m, 2H), 2.08-1.87 (m, 4H), 1.48-1.21 (m, 4H), 0.96 (t, J = 7.4 Hz, 3H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 179.8, 103.9, 95.6, 32.8, 32.3, 29.8, 27.0, 22.4, 22.3, 14.0, 13.4; IR (neat) ν = 2962, 2931, 2873, 1961, 1712, 1412, 1298, 1254 cm^{-1}; MS (70 ev, EI) *m/z* (%) 196 (M^+, 1.01), 154 (M^+-C_2H_2O, 100)[2]; HRMS Calcd for $C_{12}H_{20}O_2$: 196.1458; Found: 196.1457.

(6) Preparation of 4-butylhexa-4,5-dienoic acid (1f)

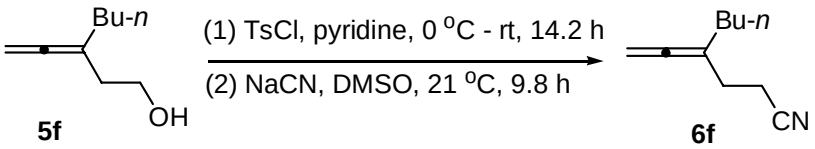
(a) Synthesis of 3-butylhexa-4,5-dien-1-ol (5f)



4f **5f**

Following the procedure for the preparation of **5a**, the reaction of hept-2-yn-ol (**4f**) (5.6 g, 0.05 mol), EtCOOH (1 mL, d = 0.99 g/mL, 0.99 g, 0.013 mol), and $MeC(OEt)_3$ (28 mL, d = 0.876 g/mL, 24.53 g, 0.15 mol) afforded ethyl 3-butylpenta-3,4-dienoate (5.8 g, crude yield 64%). The product was used in the next step without further characterization. A solution of ester (5.7 g, 0.031 mol) in anhydrous Et_2O (60 mL) was treated with $LiAlH_4$ (1.35 g, 0.035 mol) in anhydrous Et_2O (40 mL) to afford **5f** (3.8 g, 87%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.76-4.71 (m, 2H), 3.74 (t, J = 6.2 Hz, 2H), 2.24-2.17 (m, 2H), 1.99-1.92 (m, 2H), 1.66 (br, 1H), 1.47-1.27 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H). This compound was used in the next step without further characterization.

(b) Synthesis of 4-butylocta-4,5-dienenitrile (6f)

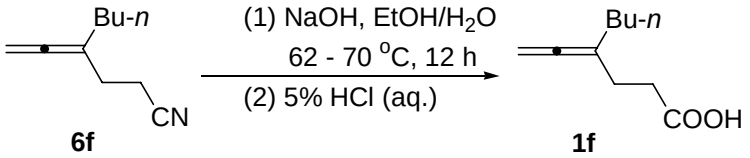


5f **6f**

Following the procedure for the preparation of **6a**, the reaction of **5f** (2.8065 g, 0.020 mol), *p*-TsCl (11.5 g, 0.060 mol), and anhydrous pyridine (30 mL) afforded the tosylate, which was used in the next step without further purification. The reaction of tosylate prepared above and NaCN (1.1860 g, 0.024 mol) in anhydrous DMSO (25 mL) afforded **6f** (1.5671 g, the combined yield from **5f** to **6f** is 52%): liquid, ^{1}H NMR

(400 MHz, $CDCl_3$) δ 4.89-4.81 (m, 2H), 2.44 (t, *J* = 7.4 Hz, 2H), 2.29-2.21 (m, 2H), 1.99-1.92 (m, 2H), 1.46-1.29 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H). This compound was used in the next step without further characterization.

(c) Synthesis of 4-butylhexa-4,5-dienoic acid (1f)

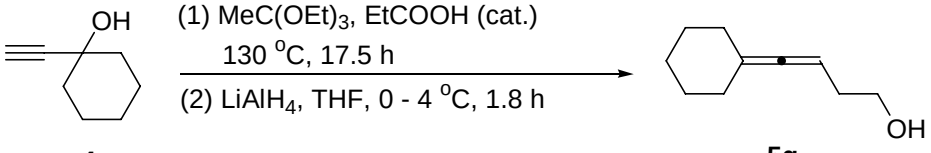


6f **1f**

Following the procedure for the preparation of **1a**, the reaction of 4-butylocta-4,5-dienenitrile (0.9865 g, 6.6 mmol), ethanol (15 mL), and aqueous NaOH solution (4.0 g in 5.2 mL of H_2O, 100 mmol) afforded **1f** (0.9768 g, 87%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (bs, COOH, 1H), 4.76-4.66 (m, 2H), 2.51 (t, *J* = 7.6 Hz, 2H), 2.26-2.19 (m, 2H), 2.00-1.92 (m, 2H), 1.48-1.23 (m, 4H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.9, 180.0, 102.3, 77.2, 32.2, 32.1, 29.6, 26.2, 22.3, 13.9; IR (neat) ν = 3048, 2958, 2928, 1958, 1710, 1429, 1285, 1217 cm^{-1}; MS (70 ev, EI) *m/z* (%) 168 (M^+, 3.91), 126 (M^+-C_2H_2O, 60.23)[2], 81 (100); HRMS Calcd for $C_{10}H_{16}O_2$ (M^+): 168.1145; Found: 168.1147.

(7) Preparation of 5-cyclohexylidenepent-4-enoic acid (1g)

(a) Synthesis of 4-cyclohexylidenebut-3-en-1-ol (5g)

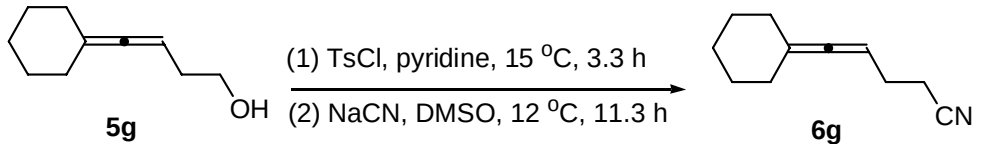


4g **5g**

Following the procedure for the preparation of **5a**, the reaction of 1-ethynylcyclohexanol (**4g**) (3.65 g, 0.03 mol), EtCOOH (this compound was added in three portions: 0.8 mL, 0.5 mL, 0.5 mL, total 1.8 mL, *d* = 0.99 g/mL, 1.78 g, 0.024 mol), and $MeC(OEt)_3$ (21.5 mL, *d* = 0.876 g/mL, 18.83 g, 0.12 mol) afforded ethyl 4-cyclohexylidenebut-3-enoate (4.6602 g, crude yield 76%). The product was used in the next step without further characterization. A solution of ester (4.6365 g, 0.024 mol) in anhydrous THF (10 mL) was treated with $LiAlH_4$ (1.1263 g, 0.029 mol) in anhydrous THF (20 mL) to afford **5g** (3.2386 g, 89%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.00-4.91 (m, 1H), 3.67 (t, *J* = 6.4 Hz, 2H), 2.21 (q, *J* = 6.0 Hz, 2H), 2.09 (t,

J = 5.8 Hz, 4H), 1.81 (s, 1H), 1.66-1.43 (m, 6H). This compound was used in the next step without further characterization.

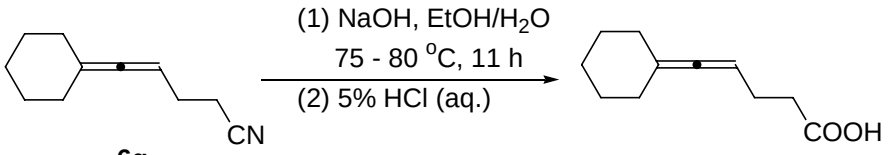
(b) Synthesis of 5-cyclohexylidenepent-4-enenitrile (6g)



5g **6g**

Following the procedure for the preparation of **6a**, the reaction of **5g** (3.2063 g, 0.021 mol), *p*-TsCl (12.18 g, 0.064 mol), and anhydrous pyridine (30 mL) afforded the tosylate, which was used in the next step without further purification. The reaction of tosylate prepared above and NaCN (1.2325 g, 0.025 mmol) in anhydrous DMSO (25 mL) afforded **6g** (2.5853 g, the combined yield from **5g** to **6g** is 76%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10-5.00 (m, 1H), 2.42 (t, J = 7.0 Hz, 2H), 2.29 (q, J = 6.4 Hz, 2H), 2.19-2.15 (m, 4H), 1.65-1.56 (m, 4H), 1.56-1.45 (m, 2H). This compound was used in the next step without further characterization.

(c) Synthesis of 5-cyclohexylidenepent-4-enoic acid (1g)

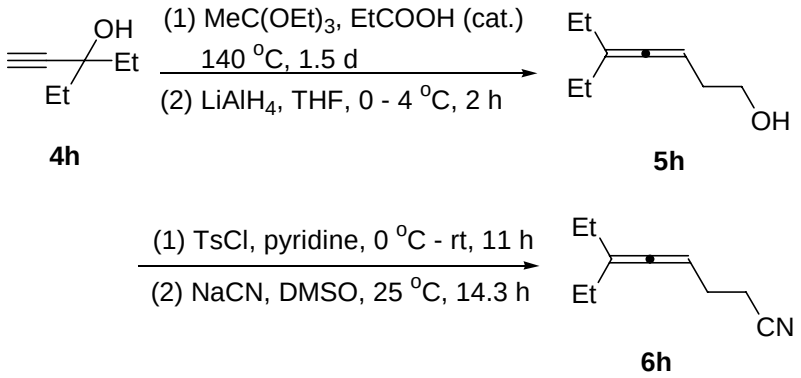


6g **1g**

Following the procedure for the preparation of **1a**, the reaction of 5-cyclohexylidenepent-4-enenitrile (0.9860 g, 6.1 mmol), ethanol (15 mL), and NaOH solution (4 g in 5.2 mL of H_2O, 100 mmol) afforded **1g** (0.8426 g, 76%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.24 (bs, COOH, 1H), 5.07-5.01 (m, 1H), 2.46 (t, J = 7.0 Hz, 2H), 2.31-2.23 (m, 2H), 2.13-2.02 (m, 4H), 1.63-1.42 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 179.8, 104.5, 87.1, 33.0, 31.5, 27.3, 26.1, 23.8; IR (neat) ν = 3030, 2927, 2853, 1966, 1712, 1446, 1263, 1211 cm^{-1}; MS (70 ev, EI) *m/z* (%) 180 (M^+, 26.60), 138 (M^+-C_2H_2O, 100)[2]; HRMS Calcd for $C_{11}H_{16}O_2$ (M^+): 180.1145, Found: 180.1146.

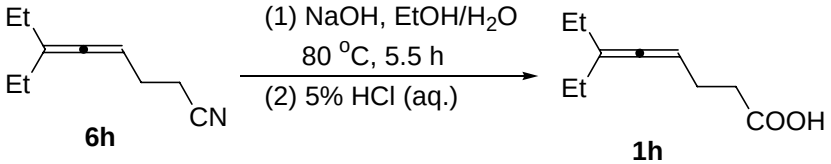
(8) Preparation of 6-ethylocta-4,5-dienoic acid (1h)

(a) Synthesis of 6-ethylocta-4,5-dienenitrile (6h)



Following the procedure for the preparation of **5a**, the reaction of 3-ethylpentyn-3-ol (**4h**) (7.8414 g, 0.07 mol), EtCOOH (1.5 mL, d = 0.99 g/mL, 1.49 g, 0.020 mol), and $MeC(OEt)_3$ (38.8 mL, d = 0.876 g/mL, 33.99 g, 0.21 mol) afforded ethyl 5-ethylhepta-3,4-dienoate (8.3190 g, crude yield 65%). The product was used in the next step without further characterization. A solution of this ester (7.9470 g, 0.044 mol) in anhydrous THF (10 mL) was treated with $LiAlH_4$ (1.8440 g, 0.048 mol) in anhydrous THF (30 mL) to afford **5h** (4.6047 g, crude yield 75%). The product was used in the next step without further characterization. Following the procedure for the preparation of **6a**, the reaction of **5h** (4.6047 g, 0.33 mol), *p*-TsCl (18.9 g, 0.099 mol), and anhydrous pyridine (30 mL) afforded the tosylate, which was used in the next step without further purification. The reaction of tosylate prepared above and NaCN (1.9387 g, 0.04 mmol) in anhydrous DMSO (45 mL) afforded **6h** (2.8487 g, the combined yield from **5h** to **6h** is 58%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.27-5.21 (m, 1H), 2.42-2.37 (m, 2H), 2.36-2.26 (m, 2H), 2.02-1.93 (m, 4H), 0.99 (t, J = 7.2 Hz, 6H). This compound was used in the next step without further characterization.

(b) Synthesis of 6-ethylocta-4,5-dienoic acid (1h)

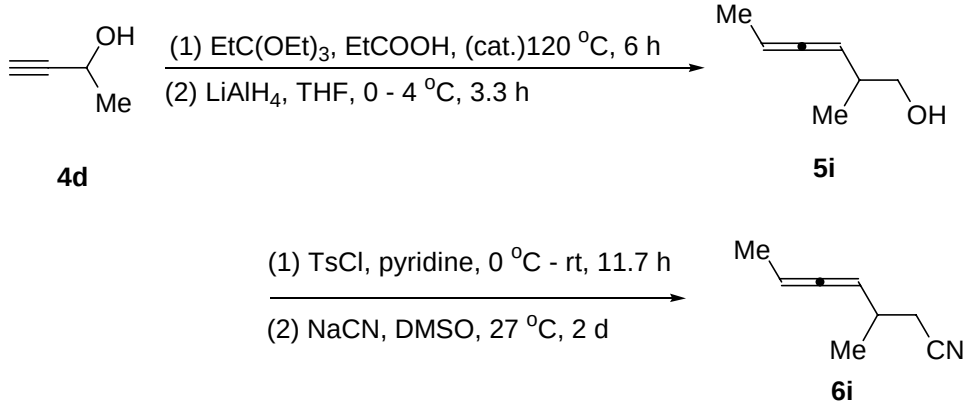


Following the procedure for the preparation of **1a**, the reaction of 6-ethylocta-4,5-dienenitrile (1.0090 g, 6.7 mmol), ethanol (15 mL) and NaOH solution (4 g in 5.2 mL of H_2O, 100 mmol) afforded **1g** (0.7686 g, 68%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.43 (bs, COOH, 1H), 5.30-5.18 (m, 1H), 2.45 (t, J = 7.2

Hz, 2H), 2.35-2.24 (m, 2H), 2.00-1.87 (m, 4H), 0.97 (t, J = 7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 179.7, 110.0, 91.3, 33.2, 25.6, 24.1, 12.2; IR (neat) ν = 3034, 2966, 2933, 1962, 1713, 1456, 1435, 1411, 1281, 1250, 1205, 1171 cm^{-1}; MS (70 ev, EI) *m/z* (%) 168 (M^+, 52.13), 126 (M^+-C_2H_2O, 98.25)[2], 93 (100); HRMS Calcd for $C_{10}H_{16}O_2$ (M^+): 168.1145; Found: 168.1149.

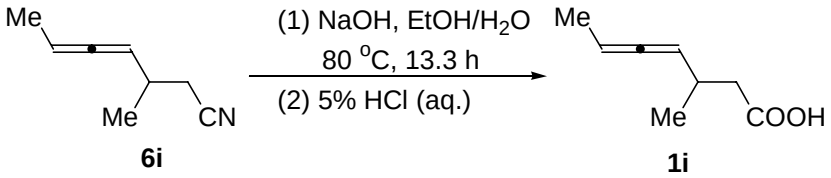
(9) Preparation of 3-methylhepta-4,5-dienoic acid (1i)

(a) Synthesis of 3-methylhepta-4,5-dienenitrile (6i)



Following the procedure for the preparation of **5a**, the reaction of but-3-yn-2-ol (**4d**) (7.1565 g, 0.10 mol), EtCOOH (1.5 mL, d = 0.99 g/mL, 1.49 g, 0.020 mol), and $EtC(OEt)_3$ (53.0 g, 0.30 mol) afforded ethyl 2-methylhexa-3,4-dienoate (15.8503 g). The product was used in the next step without further characterization. A solution of this ester (15.8503 g, 0.093 mol) in anhydrous THF (10 mL) was treated with $LiAlH_4$ (3.5139 g, 0.093 mol) in anhydrous THF (50 mL) to afford **5i** (7.2193 g, the crude combined yield from **4d** to **5i** is 63%). The product was used in the next step without further characterization. Following the procedure for the preparation of **6a**, the reaction of **5i** (6.9766, 0.062 mol), *p*-TsCl (35.7 g, 0.19 mol), and anhydrous pyridine (30 mL) afforded the tosylate, which was used in the next step without further purification. The reaction of tosylate (4.9546 g, 0.019 mol) prepared above and NaCN (1.1100 g, 0.02 mmol) in anhydrous DMSO (30 mL) afforded **6i** (1.2498 g, the combined yield from **5i** to **6i** is 17%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30-5.20 (m, 1H), 5.14-5.07 (m, 1H), 2.60-2.49 (m, 1H), 2.45-2.28 (m, 2H), 1.69 (dd, J_1 = 6.6 Hz, J_2 = 3 Hz, 2H), 1.19-1.15 (m, 3 H). This compound was used in the next step without further characterization.

(b) Synthesis of 3-methylhepta-4,5-dienoic acid (1i)

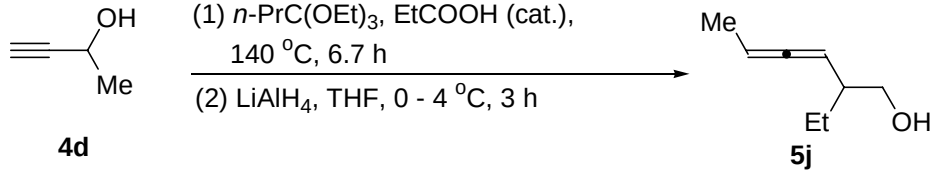


6i **1i**

Following the procedure for the preparation of **1a**, the reaction of 3-methylhepta-4,5-dienenitrile (1.2498 g, 10.3 mmol), ethanol (15 mL), and NaOH solution (4 g in 5.2 mL of H_2O, 100 mmol) afforded **1i** (0.8935 g, 62%, *dr* = 2.0/1, the *dr* value of **1i** was determined by inverse gated decoupling ^{13}C NMR analysis[3]): liquid, ^1H NMR (400 MHz, $CDCl_3$) δ 9.84 (bs, COOH, 1H), 5.21-5.05 (m, 2H), 2.74-2.60 (m, 1H), 2.50-2.40 (m, 1H), 2.34-2.24 (m, 1H), 1.67-1.58 (m, 3H), 1.10-1.05 (m, 3H); IR (neat) ν = 3088, 3037, 2967, 2929, 1964, 1709, 1412, 1295, 1229, 1199, 1074 cm^{-1}; MS (70 ev, EI) *m/z* (%) 140 (M^+, 14.06), 98 (M^+-C_2H_2O, 100)[2]; Anal. Cacld for: $C_8H_{12}O_2$ (%) C, 68.54; H, 8.63; Found: C, 68.53; H, 8.59.

(10) Preparation of 3-ethylhepta-4,5-dienoic acid (1j)

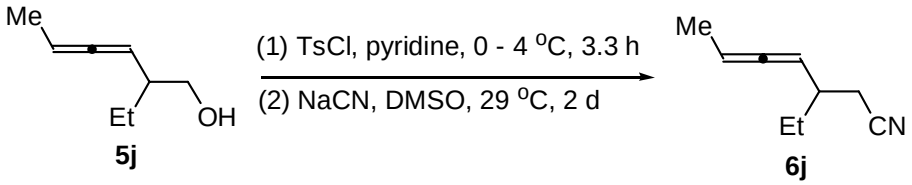
(a) Synthesis of 2-ethylhexa-3,4-dien-1-ol (5j)



4d **5j**

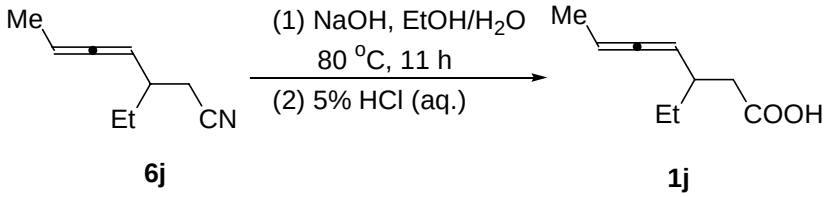
Following the procedure for the preparation of **5a**, the reaction of but-3-yn-2-ol (**4d**) (2.2 g, 0.031 mol), EtCOOH (1.5 mL, *d* = 0.99 g/mL, 1.49 g, 0.020 mol), and *n*-$PrC(OEt)_3$ (17.1 g, 0.090 mol) afforded ethyl 2-ethylhexa-3,4-dienoate (3.9910 g). The product was used in the next step without further characterization. A solution of ester (3.9910 g, 0.024 mol) in anhydrous THF (10 mL) was treated with $LiAlH_4$ (0.9915 g, 0.026 mol) in anhydrous THF (30 mL) to afford **5j** (2.9088 g, the combined yield from **4d** to **5j** is 74%): liquid, ^1H NMR (400 MHz, $CDCl_3$) δ 5.17-5.09 (m, 1H), 4.99-4.89 (m, 1H), 3.62-3.56 (m, 1H), 3.52-3.46 (m, 1H), 2.18-2.08 (m, 1H), 1.67 (dd, J_1 = 7.0 Hz, J_2 = 3.0 Hz, 3H), 1.63 (s, 1H), 1.52-1.42 (m, 1H), 1.37-1.24 (m, 1H), 0.97-0.91 (m, 3H). This compound was used in the next step without further characterization.

(b) Synthesis of 3-ethylhepta-4,5-dienenitrile (6j)



Following the procedure for the preparation of **6a**, the reaction of **5j** (2.9088 g, 0.023 mol), *p*-TsCl (13.19 g, 0.069 mol), and anhydrous pyridine (30 mL) afforded the tosylate, which was used in the next step without further purification. The reaction of tosylate prepared above and NaCN (1.1147 g, 0.023 mmol) in anhydrous DMSO (30 mL) afforded **6j** (1.9588 g, the combined yield from **5j** to **6j** is 63%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.25-5.16 (m, 1H), 5.07-4.98 (m, 1H), 2.40-2.35 (m, 2H), 2.34-2.24 (m, 1H), 1.67 (dd, J_1 = 7.0 Hz, J_2 = 3.0 Hz, 3H), 1.60-1.40 (m, 2H), 0.97-0.89 (m, 3H).

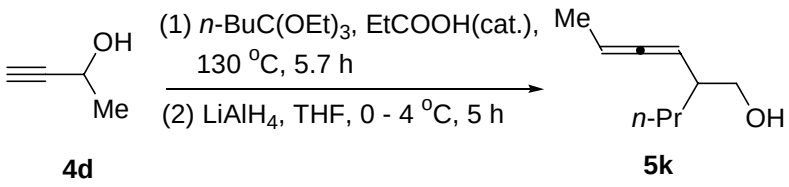
(c) Synthesis of 3-ethylhepta-4,5-dienoic acid (1j)



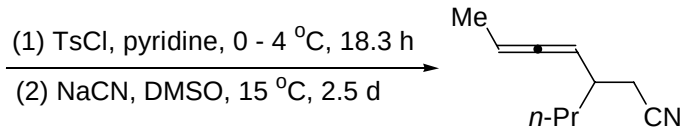
Following the procedure for the preparation of **1a**, the reaction of 3-ethylhepta-4,5-dienenitrile (0.9135 g, 6.8 mmol), ethanol (15 mL), and NaOH solution (4.0 g in 5.2 mL of H_2O, 100 mmol) afforded **1j** (0.7178 g, 69%, *dr* = 2.2/1, the *dr* value of **1j** was determined by inverse gated decoupling ^{13}C NMR analysis[3]): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.78 (bs, COOH, 1H), 5.18-5.08 (m, 1H), 5.08-4.99 (m, 1H), 2.57-2.41 (m, 1H), 2.41-2.33 (m, 2H), 1.66-1.60 (m, 3H), 1.53-1.34 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); IR (neat) ν = 3030, 2964, 2926, 1964, 1713, 1461, 1412, 1291, 1223, 1188 cm^{-1}; MS (70 ev, EI) *m/z* (%) 154 (M^+, 20.53), 125 (M^+-C_2H_5, 22.00), 112 (M^+-C_2H_2O, 95.71)[2], 79 (100); Anal. Cacld for: $C_9H_{14}O_2$ (%) C, 70.10; H, 9.15; Found: C, 70.13; H, 9.16.

(11) Preparation of 3-propylhepta-4,5-dienoic acid (1k)

(a) Synthesis of 3-propylhepta-4,5-dienenitrile (6k)



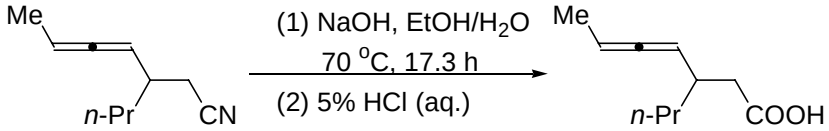
4d **5k**



6k

Following the procedure for the preparation of **5a**, the reaction of but-3-yn-2-ol (**4d**) (3.5 g, 0.05 mol), EtCOOH (1 mL, *d* = 0.99 g/mL, 0.99 g, 0.013 mol), and *n*-BuC(OEt)$_3$ (30 mL, 0.14 mol) afforded ethyl 2-propylhexa-3,4-dienoate (8.1517 g, crude yield 89%). The product was used in the next step without further characterization. A solution of this ester (7.3006 g, 0.040 mol) in anhydrous THF (30 mL) was treated with $LiAlH_4$ (2.0026 g, 0.053 mol) in anhydrous THF (20 mL) to afford **5k** (3.8356 g, crude yield 68%). The product was used in the next step without further characterization. Following the procedure for the preparation of **6a**, the reaction of **5k** (5.3111 g, 0.038 mol), *p*-TsCl (18 g, 0.095 mol), and anhydrous pyridine (30 mL) afforded the tosylate, which was used in the next step without further purification. The reaction of tosylate prepared above and NaCN (2.2840 g, 0.047 mmol) in anhydrous DMSO (35 mL) afforded **6k** (4.9366 g, the combined yield from **5k** to **6k** is 87%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.28-5.16 (m, 1H), 5.08-4.98 (m, 1H), 2.45-2.34 (m, 3H), 1.68 (dd, J_1 = 7.2 Hz, J_2 = 3.3 Hz, 3H), 1.53-1.24 (m, 4H), 0.92 (t, *J* = 7.1 Hz, 3H). This compound was used in the next step without further characterization.

(b) Synthesis of 3-propylhepta-4,5-dienoic acid (1k)



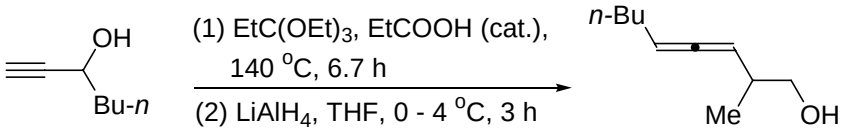
6k **1k**

Following the procedure for the preparation of **1a**, the reaction of 3-propylhepta-4,5-dienenitrile (1.0073 g, 6.8 mmol), ethanol (15 mL), and NaOH solution (4.0 g in 5.2 mL of H_2O, 100 mmol) afforded **1k** (0.6690 g, 59%, *dr* = 2.2/1,

the *dr* value of **1k** was determined by inverse gated decoupling ^{13}C NMR analysis[3]): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.06 (bs, COOH, 1H), 5.19-4.98 (m, 2H), 2.62-2.47 (m, 1H), 2.43-2.32 (m, 2H), 1.66-1.58 (m, 3H), 1.46-1.26 (m, 4H), 0.95-0.85 (m, 3H); IR (neat) ν = 3030, 2959, 2929, 2873, 1965, 1709, 1412, 1296, 1236, 1184 cm^{-1}; MS (70 ev, EI) *m/z* (%) 168 (M^+, 2.99), 126 (M^+-C_2H_2O, 100)[2]; HRMS Calcd for $C_{10}H_{16}O_2$ (M^+): 168.1145; Found: 168.1143.

(12) Preparation of 3-methyldeca-4,5-dienoic acid (1l)

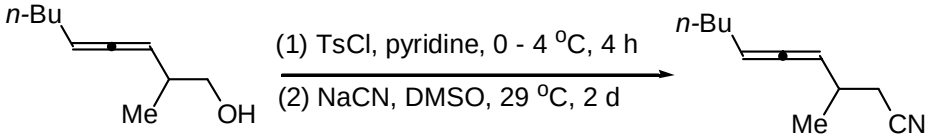
(a) Synthesis of 2-methylnona-3,4-dien-1-ol (5l)



4c **5l**

Following the procedure for the preparation of **5a**, the reaction of heptyn-3-ol (**4c**) (3.2 g, 0.03 mol), EtCOOH (1.5 mL, *d* = 0.99 g/mL, 1.49 g, 0.020 mol), and $EtC(OEt)_3$ (15.8 g, 0.09 mol) afforded ethyl 2-methylnona-3,4-dienoate (6.3281 g). The product was used in the next step without further characterization. A solution of this ester (6.3281 g, 0.032 mol) in anhydrous THF (10 mL) was treated with $LiAlH_4$ (1.3457 g, 0.035 mol) in anhydrous THF (30 mL) to afford **5l** (3.7854 g, the combined yield from **4c** to **5l** is 87%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21-5.13 (m, 1H), 5.08-5.02 (m, 1H), 3.55-3.44 (m, 2H), 2.39-2.30 (m, 1H), 2.03-1.95 (m, 2H), 1.73 (s, 1H), 1.43-1.29 (m, 4H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H). This compound was used in the next step without further characterization.

(b) Synthesis of 3-methyldeca-4,5-dienenitrile (6l)

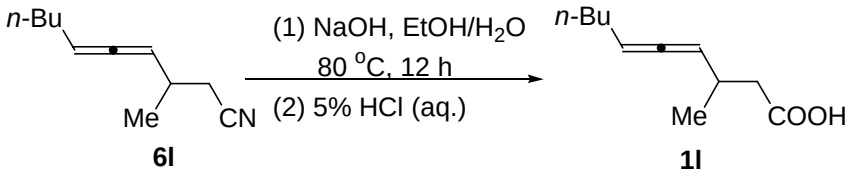


5l **6l**

Following the procedure for the preparation of **6a**, the reaction of **5l** (3.7854 g, 0.025 mol), *p*-TsCl (14.1 g, 0.074 mol), and anhydrous pyridine (30 mL) afforded the tosylate, which was used in the next step without further purification. The reaction of tosylate prepared above and NaCN (1.1969 g, 0.025 mmol) in anhydrous DMSO (30

mL) afforded **6l** (3.4896 g, the combined yield from **5l** to **6l** is 86%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35-5.22 (m, 1H), 5.20-5.09 (m, 1H), 2.62-2.48 (m, 1H), 2.46-2.26 (m, 2H), 2.10-2.95 (m, 2H), 1.48-1.28 (m, 4H), 1.29-1.32 (m, 3H), 0.90 (t, *J* = 6.8 Hz, 3H). This compound was used in the next step without further characterization.

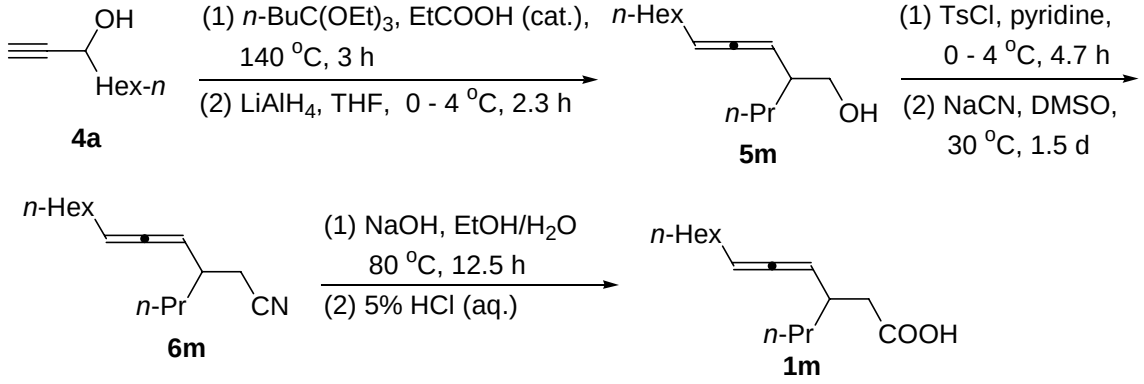
(c) Synthesis of 3-methyldeca-4,5-dienoic acid (1l)



6l **1l**

Following the procedure for the preparation of **1a**, the reaction of 3-methyldeca-4,5-dienenitrile (0.9977 g, 6.1 mmol), ethanol (15 mL), and NaOH solution (4 g in 5.2 mL of H_2O, 100 mmol) afforded **1l** (0.7856 g, 71%, *dr* = 3.1/1, *dr* value of **1l** was determined by inverse gated decoupling ^{13}C NMR analysis[3]): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (bs, COOH, 1H), 5.23-5.09 (m, 2H), 2.73-2.58 (m, 1H), 2.52-2.37 (m, 1H), 2.36-2.21 (m, 1H), 2.03-1.91 (m, 2H), 1.43-1.27 (m, 4H), 1.01-1.06 (m, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); IR (neat) ν = 3082, 3032, 2961, 2929, 1962, 1711, 1458, 1410, 1293, 1230, 1198, cm^{-1}; MS (70 ev, EI) *m/z* (%) 182 (M^+, 2.24), 140 (M^+-C_2H_2O, 100)[2]; Anal. Cacld for: $C_{11}H_{18}O_2$ (%) C, 72.49; H, 9.95; Found: C, 72.45; H, 10.09.

(13)Preparation of 3-propyldodeca-4,5-dienoic acid (1m)



4a **5m** **6m** **1m**

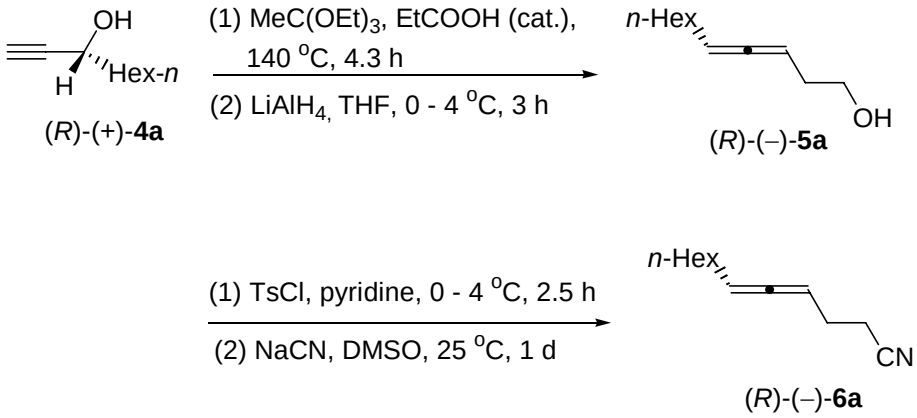
Following the procedure for the preparation of **5a**, the reaction of nonyn-3-ol (**4a**) (2.8002 g, 0.02 mol), EtCOOH (1 mL, *d* = 0.99 g/mL, 0.99 g, 0.013 mol), and

n-BuC(OEt)$_3$ (12.5 g, 0.06 mol) afforded ethyl 2-propylundeca-3,4-dienoate (7.7166 g). The product was used in the next step without further characterization. A solution of this ester (7.7166 g, 0.037 mol) in anhydrous THF (10 mL) was treated with $LiAlH_4$ (1.4006 g, 0.037 mol) in anhydrous THF (40 mL) to afford **5m** (3.3020 g, crude yield 79%). The product was used in the next step without further characterization. Following the procedure for the preparation of **6a**, the reaction of **5m** (2.1345 g, 0.010 mol), *p*-TsCl (5.81 g, 0.03 mol), and anhydrous pyridine (30 mL) afforded the tosylate, which was used in the next step without further purification. The reaction of tosylate prepared above and NaCN (0.6168 g, 0.013 mmol) in anhydrous DMSO (20 mL) afforded **6m** (1.6696 g, crude yield 75%). The product was used in the next step without further characterization. Following the procedure for the preparation of **1a**, the reaction of 3-propyldodeca-4,5-dienenitrile (0.5315 g, 2.4 mmol), ethanol (8 mL) and NaOH solution (2.0 g in 2.5 mL of H_2O, 100 mmol) afforded **1m** (0.4998 g, 87%, *dr* = 2.7/1, *dr* value of **1m** was determined by inverse gated decoupling ^{13}C NMR analysis[3]): liquid, ^1H NMR (300 MHz, $CDCl_3$) δ 10.06 (bs, COOH, 1H), 5.19-5.01 (m, 2H), 2.61-2.46 (m, 1H), 2.38 (d, *J* = 7.2 Hz, 2H), 2.04-1.86 (m, 2H), 1.49-1.18 (m, 12H), 0.98-0.80 (m, 6H); IR (neat) ν = 3028, 2958, 2928, 2857, 1962, 1710, 1466, 1409, 1379, 1294, 1184 cm^{-1}; MS (70 ev, EI) *m/z* (%) 238 (M^+, 3.17), 196 (M^+-C_2H_2O, 16.34)[2], 79 (100); Anal. Cacld for $C_{15}H_{26}O_2$ (%) C, 75.58; H, 10.99; Found: C, 75.46; H, 10.94.

Procedures for the preparation of optically active γ-allenoic acids[2] ((*R*)-(–)-1a, (*R*) -(–)-1b, (*S*)-(+)-1l, (*S*)-(+)-1m and (R_a, *R*)-(–)-1l)

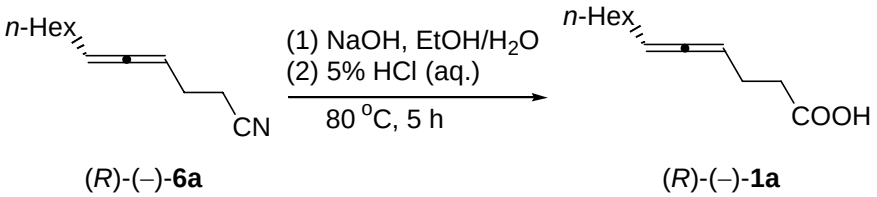
(1) Preparation of optically active γ-allenoic acid[4] ((*R*)-(–)-1a)

(a) Synthesis of (*R*)-(–)-dodeca-4,5-dienenitrile ((*R*)-(–)-6a)



Following the procedure for the preparation of **5a**, the reaction of (*R*)-(+)-nonyn-3-ol ((*R*)-(+)-**4a**) (4.0693 g, 29 mmol, 99% ee, $[\alpha]^{20}_{D}$ = +4.6 (*c* = 1.92, $CHCl_3$)), EtCOOH (1.5 mL, *d* = 0.99 g/mL, 1.49 g, 0.020 mol), and $MeC(OEt)_3$ (14.3 g, 86 mmol) afforded ethyl (*R*)-(–)-undeca-3,4-dienoate (4.1724 g). The product was used in the next step without further characterization. A solution of this ester (4.1724 g, 19.9 mmol) in THF (30 mL) was treated with $LiAlH_4$ (0.7990 g, 21 mmol) in anhydrous THF (30 mL) to afford (*R*)-(–)-**5a** (2.4345 g, the crude combined yield from (*R*)-(+)-**4a** to (*R*)-(–)-**5a** is 50%). The product was used in the next step without further characterization. Following the procedure for the preparation of **6a**, the reaction of (*R*)-(–)-**5a** (1.6055 g, 10 mmol), *p*-TsCl (5.7 g, 30 mmol), and dry pyridine (20 mL) afforded the tosylate, which was used in the next step without further purification. The reaction of tosylate prepared above and NaCN (0.5584 g, 11.4 mmol) in anhydrous DMSO (20 mL) afforded (*R*)-(–)-**6a** (1.3584 g, the combined yield from (*R*)-(–)-**5a** to (*R*)-(–)-**6a** is 66%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.32-5.20 (m, 1H), 5.20-5.08 (m, 1H), 2.42 (t, *J* = 6.8 Hz, 2H), 2.35-2.24 (m, 2H), 2.06-1.95 (m, 2H), 1.47-1.16 (m, 8H), 0.87 (t, *J* = 6.3 Hz, 3H). $[\alpha]^{20}_{D}$ = -69.2 (*c* = 0.99, $CHCl_3$) This compound was used in the next step without further characterization.

(b) Synthesis of (*R*)-(–)-dodeca-4,5-dienoic acid ((*R*)-(–)-1a)

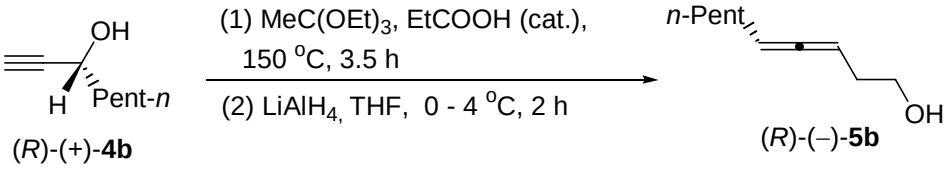


Following the procedure for the preparation of **1a**, the reaction of (*R*)-(–)-**6a**

(0.7106 g, 4.0 mmol), ethanol (10 mL), and NaOH solution (3.0 g in 4 mL of H_2O, 75 mmol) afforded (*R*)-(–)-**1a** (0.5703 g, 72%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.45 (bs, COOH, 1H), 5.21-5.08 (m, 2H), 2.53-2.41 (m, 2H), 2.38-2.22 (m, 2H), 2.01-1.87 (m, 2H), 1.44-1.16 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H). $[\alpha]^{20}_D$ = -71.4 (*c* = 1.06, $CHCl_3$).

(2) Preparation of optically active γ-allenoic acid ((*R*)-(–)-1b)

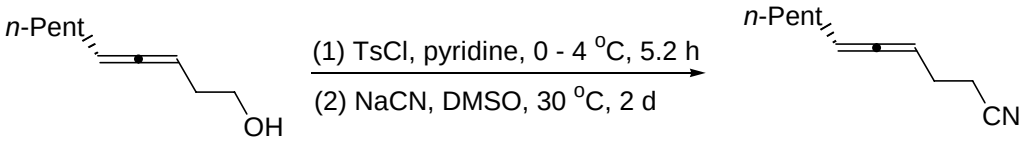
(a) Synthesis of (*R*)-(+)-deca-3,4-dien-1-ol ((*R*)-(–)-5b)



(*R*)-(+)-**4b** (*R*)-(–)-**5b**

Following the procedure for the preparation of **5a**, the reaction of (*R*)-(+)-octyn-3-ol ((*R*)-(+)-**4b**) (3.9319 g, 0.031 mol, 97% ee, $[\alpha]^{20}_D$ = +6.6 (*c* = 1.25, $CHCl_3$)), EtCOOH (0.7 mL, 0.99 g/mL, 0.69 g, 0.009 mol), and $MeC(OEt)_3$ (17 mL, *d* = 0.876 g/mL, 14.89 g, 90 mmol) afforded ethyl (*R*)-(–)-deca-3,4-dienoate (6.0548 g). The product was then used in the next step without further purification. A solution of this ester (6.0548 g, 30 mmol) in THF (30 mL) was treated with $LiAlH_4$ (1.4119 g, 36 mmol) in dry THF (30 mL) to afford (*R*)-(–)-**5b** (3.6950 g, the combined yield from (*R*)-(–)-**4b** to (*R*)-(–)-**5b** is 78%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21-5.04 (m, 2H), 3.77-3.64 (m, 2H), 2.31-2.18 (m, 2H), 2.06-1.94 (m, 2H), 1.63 (br, 1H), 1.45-1.24 (m, 6H), 0.88 (t, *J* = 7.2 Hz, 3H). $[\alpha]^{20}_D$ = -67.4 (*c* = 1.13, $CHCl_3$). This compound was used in the next step without further characterization.

(b) Synthesis of (*R*)-(–)-undeca-4,5-dienenitrile ((*R*)-(–)-6b)

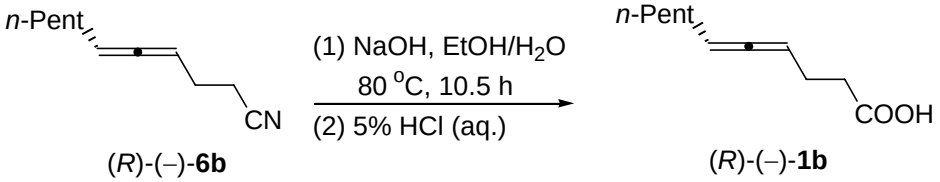


(*R*)-(–)-**5b** (*R*)-(–)-**6b**

Following the procedure for the preparation of **6a**, the reaction of (*R*)-(–)-**5b** (3.2 g, 20 mmol), *p*-TsCl (11.9 g, 60 mmol), and dry pyridine (30 mL) afforded the tosylate, which was then used in the next step without further purification. The reaction of tosylate prepared above and NaCN (1.0988 g, 21.6 mmol) in anhydrous DMSO (40

mL) afforded (*R*)-(–)-**6b** (1.2539 g, the combined yield from (*R*)-(–)-**5b** to (*R*)-(–)-**6b** is 37%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31-5.21 (m, 1H), 5.21-5.11 (m, 1H), 2.43 (t, J = 6.8 Hz, 2H), 2.36-2.28 (m, 2H), 2.02 (qd, J_1 = 7.2 Hz, J_2 = 2.8 Hz, 2H), 1.47-1.36 (m, 2H), 1.35-1.23 (m, 4H), 0.89 (t, J = 6.6 Hz, 3H). $[\alpha]^{20}_D$ = -76.8 (c = 1.74, $CHCl_3$). This compound was used in the next step without further characterization.

(c) Synthesis of (*R*)-(–)-undeca-4,5-dienoic acid ((*R*)-(–)-1b)

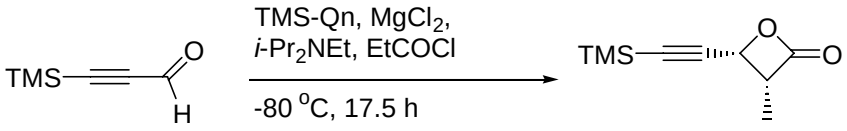


(*R*)-(–)-**6b** (*R*)-(–)-**1b**

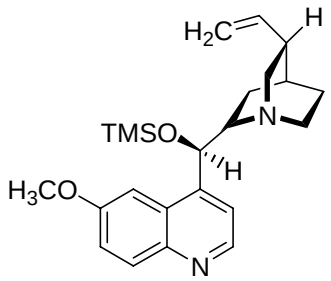
The reaction of (*R*)-(–)-**6b** (1.0121 g, 6.2 mmol), ethanol (15 mL), and NaOH solution (4.0 g in 5.3 mL of H_2O, 100 mmol) afforded (*R*)-(–)-**1b** (1.1434 g, 100%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.61 (bs, COOH, 1H), 5.20-5.11 (m, 2H), 2.54-2.42 (m, 2H), 2.35-2.24 (m, 2H), 2.01-1.92 (m, 2H), 1.44-1.34 (m, 2H), 1.34-1.20 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H). $[\alpha]^{20}_D$ = -76.7 (c = 1.05, $CHCl_3$).

(3) Preparation of (*S*)-3-methyldeca-4,5-dienoic acid ((*S*)-(+)-1l)

(a) Synthesis of (3*R*, 4*R*)-(–)-3-methyl-4-(trimethylsilyl)ethynyloxetan-2-one ((3*R*, 4*R*)-(–)-8a)[5]



7 (3*R*, 4*R*)-(–)-**8a**

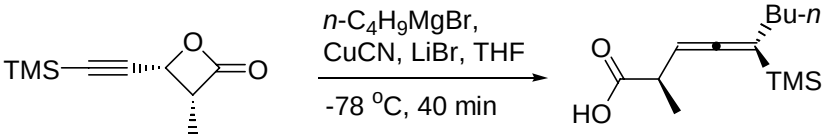


TMS-Qn

To a suspension of $MgCl_2$ (0.7614 g, 8 mmol) in 12 mL of anhydrous diethyl ether was added a solution of *N*,*N*-diisopropylethylamine (2.49 g, 20 mmol) and *O*-trimethylsilylquinine (0.3402 g, 0.8 mmol) in 25 mL of anhydrous CH_2Cl_2. Then a

solution of **7**[6] (1.0107 g, 8 mmol) in 5 mL of anhydrous CH_2Cl_2 was added at -80 °C. After being stirred at -80 °C for 40 min, a solution of propionyl chloride (1.5348 g, 17 mmol) in 5 mL of anhydrous CH_2Cl_2 was then added over 3 h by a syringe pump at this temperature. The reaction mixture was stirred for 14.5 h at −80 °C and then quenched by adding a saturated aqueous NH_4Cl solution (25 mL). The resulting mixture was extracted with diethyl ether (200 mL × 3) and the combined organic extracts were washed successively with H_2O and brine, dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether (30-60 °C): ethyl ether = 10: 1) to afford (3*R*, 4*R*)-(–)-**8a** as a colorless oil (1.0794 g, 73%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 (d, *J* = 6.4 Hz, 1H), 3.92-3.81 (m, 1H), 1.42 (d, *J* = 7.6 Hz, 3H), 0.21 (s, 9H). $[\alpha]^{20}_D$ = -12.9 (*c* = 1.26, $CHCl_3$).

(b) Synthesis of (*R*$_a$, *R*)-(–)-2-methyl-5-(trimethylsilyl)nona-3,4-dienoic acid ((*R*$_a$, *R*)-9a)

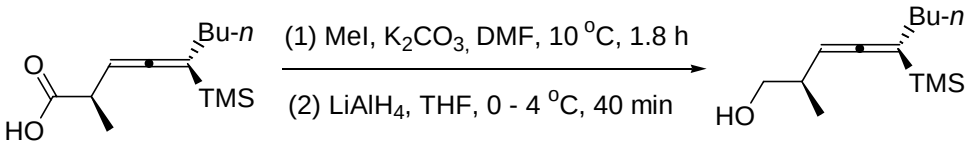


(3*R*, 4*R*)-(–)-**8a** (*R*$_a$, *R*)-(+)-**9a**

1,2-Dibromoethane (60 μL, 0.7 mmol) was added to a mixture of magnesium turnings (0.8477 g, 35 mmol) in anhydrous THF (10 mL) under nitrogen. Upon the initiation of the Grignard reaction, a solution of *n*-BuBr (2.057 g, 15 mmol) in THF (25 mL) was then added dropwise over 15 min at rt. After being stirred for 30 min, the resulting Grignard reagent solution (14 mL, 6.02 mmol) was added dropwise to a mixture of (3*R*, 4*R*)-(–)-**8a** (365.2 mg, 2.0 mmol), CuCN (18.8 mg, 0.2 mmol), and anhydrous lithium bromide (40.5 mg, 0.46 mmol) in 20 mL of anhydrous THF at –78 °C within 20 min. After being stirred at –78 °C for additional 20 min, the reaction was quenched with a saturated aqueous NH_4Cl solution (50 mL). The resulting mixture was extracted with ethyl acetate (200 mL × 2) and the combined organic extracts were successively washed with H_2O and brine, dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash chromatography on silica gel

(petroleum ether/ethyl acetate = 40/1 to 5/1) to afford (R_a, *R*)-(+)-**9a** as a colorless oil (397.6 mg, 83%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.30 (bs, 1H), 5.13-4.90 (m, 1H), 3.20-2.97 (m, 1H), 1.96 (td, J_1 = 7.4 Hz, J_2 = 3.0 Hz, 2H), 1.46-1.27 (m, 4H), 1.24 (d, *J* = 6.9 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.08 (s, 9H). $[\alpha]^{20}_D$ = +22.3 (*c* = 1.53, $CHCl_3$). This compound was used in the next step without further characterization.

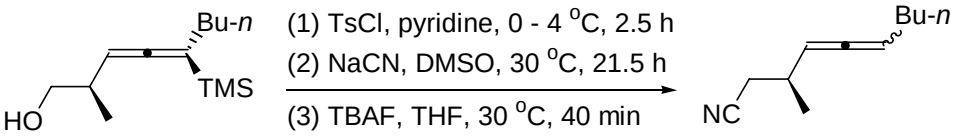
(c) Synthesis of (*R*$_a$, *R*)-(–)-2-methyl-5-(trimethylsilyl)nona-3,4-dien-1-ol ((*R*$_a$, *R*)-(–)-10a)



(R_a, *R*)-(+)-**9a** (R_a, *R*)-(–)-**10a**

To a solution of (R_a, *R*)-(+)-**9a** (1.0191 g, 4.2 mmol) in DMF (10 mL) were added K_2CO_3 (1.1472 g, 8.3 mmol) and MeI (0.42 mL, 6.8 mmol) sequentially. The resulting mixture was then stirred for 105 min at 10 °C. After being stirred at this temperature, the resulting mixture was quenched with 5 mL of H_2O and extracted with ethyl ether (50 mL × 3). The combined organic layer was washed with H_2O, brine, dried over Na_2SO_4, and filtrated. After evaporation of the solvent, chromatography on silica gel afforded (R_a, *R*)-methyl 2-methyl-5-(trimethylsilyl)nona-3,4-dienoate (0.9813 g, crude yield 91%). It was used in the next step without further purification. Following the procedure for the preparation of (*R*)-**5a,** a solution of ester (0.9484 g, 3.7 mmol) in anhydrous THF (15 mL) was added to a suspension of $LiAlH_4$ (0.1819 g, 4.8 mmol) in anhydrous THF (20 mL) to afford (R_a, *R*)-(–)-**10a** (0.7875 g, 93%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.68 (dt, J_1 = 6.6 Hz, J_2 = 3.2 Hz, 1H), 3.55-3.37 (m, 2H), 2.40-2.24 (m, 1H), 1.99-1.90 (m, 2H), 1.57 (br, 1H), 1.48-1.24 (m, 4H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.08 (s, 9H). $[\alpha]^{20}_D$ = -0.6 (*c* = 0.81, $CHCl_3$). This compound was used in the next step without further characterization.

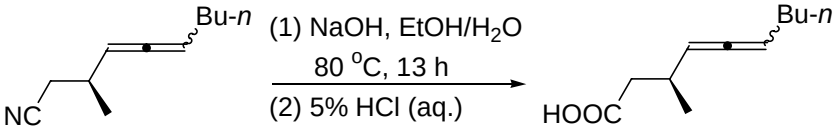
(d) Synthesis of (*S*)-(–)-3-methyldeca-4,5-dienenitrile ((*S*)-(–)-11a)



(R_a, *R*)-(–)-**10a** (*S*)-(–)-**11a**

Following the procedure for the preparation of (*R*)-**6b**, a mixture of (R_a, *R*)-(–)-**10a** (0.7625 g, 3.4 mmol) and anhydrous pyridine (15 mL) was treated with p-TsCl (in two portions: 1.9899 g + 0.9936 g, 15.7 mmol) to afford the tosylate, which was used in the next step without further purification. The reaction of the tosylate prepared above and NaCN (0.1701 g, 3.9 mmol) in anhydrous DMSO (10 mL) afforded (R_a, *S*)-3-methyl-6-trimethylsilyldeca-4,5-dienenitrile, which was used in the next step without further purification. To a solution of this nitrile in 10 mL of anhydrous tetrahydrofuran was added a solution of tetrabutylammonium fluoride in THF (3.0 mL, 1 M). The mixture was stirred at 30 °C for 40 min, diluted with ether, and washed with a saturated aqueous solution of ammonium chloride. The organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash chromatography on silica gel to afford (*S*)-(–)-**11a**[7] (195.1 mg, the combined yield from (R_a, *R*)-**10a** to (*S*)-(–)-**11a** is 35%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32-5.23 (m, 1H), 5.17-5.10 (m, 1H), 2.60-2.49 (m, 1H), 2.41 (dd, J_1 = 16.5 Hz, J_2 = 6.2 Hz, 1H), 2.32 (dd, J_1 = 16.5 Hz, J_2 = 6.8 Hz, 1H), 2.07-1.98 (m, 2H), 1.44-1.29 (m, 4H), 1.20-1.15 (m, 3H), 0.90 (t, J = 7.2 Hz, 3H). $[\alpha]^{20}_D$ = -9.1 (c = 0.51, $CHCl_3$). This compound was used in the next step without further characterization.

(e) Synthesis of (*S*)-(+)-3-methyldeca-4,5-dienoic acid ((*S*)-(+)-1l)



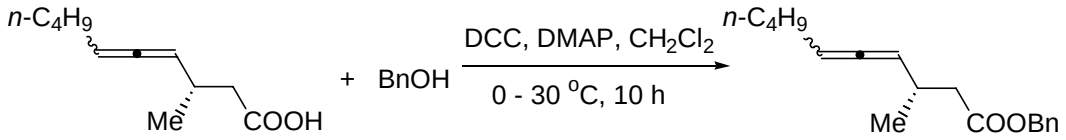
(*S*)-(–)-**11a** (*S*)-(+)-**1l**

Following the procedure of **6a**, the reaction of (*S*)-(–)-**11a** (0.1951 g, 1.2 mmol), ethanol (8 mL), and NaOH solution (2.0 g in 2.6 mL of H_2O, 50 mmol) afforded (*S*)-(+)-**1l** (0.1688 g, 77%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.94 (bs, COOH, 1H), 5.23-5.09 (m, 2H), 2.73-2.60 (m, 1H), 2.55-2.39 (m, 1H), 2.37-2.21 (m, 1H), 2.05-1.90 (m, 2H), 1.46-1.24 (m, 4H), 1.08 (d, J_1 = 6.3 Hz, 3H), 0.89 (t, J = 6.9 Hz,

3H). $[\alpha]^{20}_D$ = +19.0 (*c* = 0.93, $CHCl_3$).

The *dr* value of (*S*)-**1l** was determined after its conversion to the corresponding benzyl ester.

(f) Synthesis of benzyl (*S*)-(+)-3-methyldeca-4,5-dienoate ((*S*)-(+)-13a)

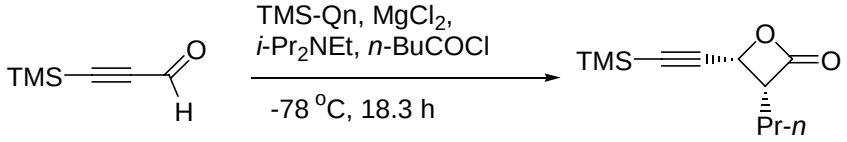


(*S*)-**1l** (*S*)-**13a**

Following the procedure for the benzylation of (R_a, *R*)-**1l**, the reaction of (*S*)-**1l** (9.8 mg, 0.05 mmol), BnOH (17.8 mg, 0.16 mmol), DMAP (5.1 mg, 0.04 mmol), and DCC (14.4 mg, 0.07 mmol) in 1 mL of CH_2Cl_2 afforded (*S*)-(+)-**13a** (12.0 mg, 82%), *dr* = 1.2/1, the *dr* value was determined by HPLC. (Conditions: Chiralcel AS-H column; rate, 0.5 mL/min; eluent, hexane/*i*-PrOH = 100/0; λ = 214 nm, t_R 27.1 (minor), 32.4 (major)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.29 (m, 5H), 5.20-5.06 (m, 4H), 2.76-2.63 (m, 1H), 2.50-2.40 (m, 1H), 2.36-2.24 (m, 1H), 2.01-1.89 (m, 2H), 1.41-1.27 (m, 4H), 1.05 (d, *J* = 6.9 Hz, 3H), 0.93-0.84 (m, 3H); IR (neat) ν = 1961, 1738, 1499, 1455, 1378, 1159 cm^{-1}; MS (70 ev, EI) *m/z* (%) 272 (M^+, 0.57), 69 (100); HRMS Calcd for $C_{18}H_{24}O_2Na$ (M^++Na): 295.1669, Found: 295.1666. $[\alpha]^{20}_D$ = +12.1 (*c* = 0.475, $CHCl_3$).

(4) Preparation of (*S*)-(+)-3-propyldodeca-4,5-dienoic acid ((*S*)-(+)-1m)

(a) Synthesis of (*3R*, *4R*)-(–)-3-propyl-4-(trimethylsilyl)ethynyloxetan-2-one ((*3R*, *4R*)-8b)

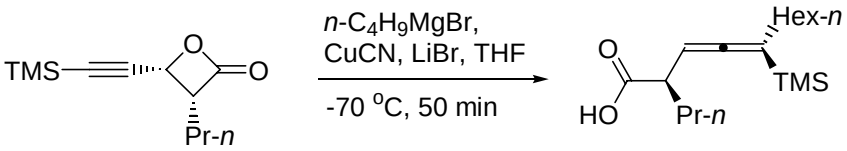


7 (3*R*, 4*R*)-(–)-**8b**

Following the procedure for the preparation of (3*R*, 4*R*)-(–)-**8a**, the reaction of $MgCl_2$ (0.9809 g, 10 mmol), anhydrous diethyl ether (25 mL), *N*,*N*-diisopropylethylamine (3.1125 g, 25 mmol), *O*-trimethylsilylquinine (0.4631 g, 1 mmol), 40 mL of anhydrous CH_2Cl_2, **7**[5] (1.3110 g, 10 mmol) in anhydrous CH_2Cl_2 (5

mL), and pentanoyl chloride (2.1073 g, 18 mmol) in anhydrous CH_2Cl_2 (5 mL) afforded (3*R*,4*R*)-(–)-**8b** (1.2938 g, 58%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 (d, *J* = 6.0 Hz, 1H), 3.79-3.69 (m, 1H), 1.93-1.81 (m, 2H), 1.55-1.40 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.21 (s, 9H). $[\alpha]^{20}_D$ = -42.5 (*c* = 1.41, $CHCl_3$). This compound was used in the next step without further characterization.

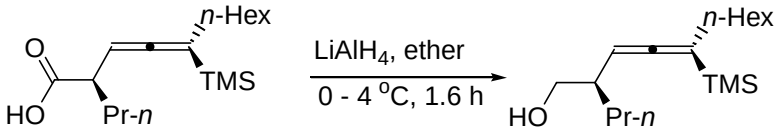
(b) Synthesis of (*R*$_a$, *R*)-(–)-2-propyl-5-(trimethylsilyl)undeca-3,4-dienoic acid ((*R*$_a$, *R*)-(–)-9b)



(3*R*, 4*R*)-(–)-**8b** (*R*$_a$, *R*)-(–)-**9b**

Following the procedure for the preparation of (*R*$_a$, *R*)-(+)-**9a**, the reaction of a solution of $C_6H_{13}MgBr$ in anhydrous THF (35 mL, 0.54 M, 19 mmol), (3*R*, 4*S*)-(–)-**8b** (1.26 g, 6.0 mmol), CuCN (52.9 mg, 0.6 mmol), and anhydrous lithium bromide (0.1193 mg, 1.4 mmol) in THF (60 mL) afforded (*R*$_a$, *R*)-(–)-**9b** (1.3238 g, 75%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.33 (bs, 1H), 4.96-4.83 (m, 1H), 3.05-2.80 (m, 1H), 2.05-1.87 (m, 2H), 1.78-1.62 (m, 1H), 1.60-1.48 (m, 1H), 1.46-1.21 (m, 10H), 0.98-0.79 (m, 6H), 0.08 (s, 9H). $[\alpha]^{20}_D$ = -39.7 (*c* = 0.61, $CHCl_3$). This compound was used in the next step without further characterization.

(c) Synthesis of (*R*$_a$, *R*)-(–)-2-propyl-5-(trimethylsilyl)undeca-3,4-dien-1-ol ((*R*$_a$, *R*)-10b)

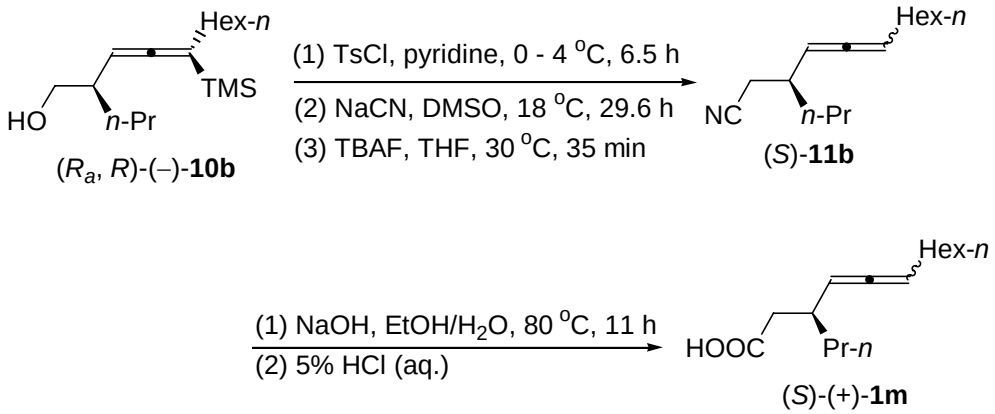


(*R*$_a$, *R*)-(–)-**9b** (*R*$_a$, *R*)-(–)-**10b**

Following the procedure for the preparation of (*R*)-**5a,** the reaction of $LiAlH_4$ (0.2059 g, 5.4 mmol) and (*R*$_a$, *R*)-**9b** (1.2627 g, 4.3 mmol) in anhydrous diethyl ether (40 mL) afforded (*R*$_a$, *R*)-**10b** (0.8388 g, 70%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.68-4.60 (m, 1H), 3.59-3.50 (m, 1H), 3.45-3.36 (m, 1H), 2.24-2.13 (m, 1H), 1.98-1.91 (m, 2H), 1.60 (s, 1H), 1.49-1.36 (m, 4H), 1.36-1.20 (m, 8H), 0.95-0.83 (m, 6H), 0.09 (s, 9H). $[\alpha]^{20}_D$ = -21.4 (*c* = 1.35, $CHCl_3$). This compound was used in the

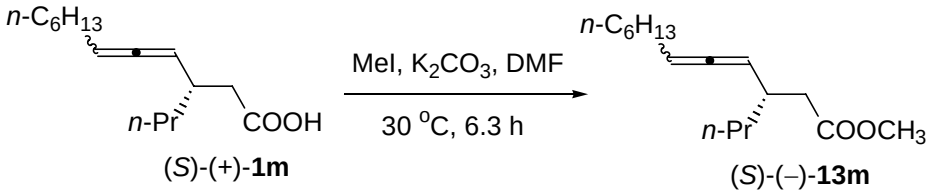
next step without further characterization.

(d) Synthesis of (*S*)-(–)-3-propyldodeca-4,5-dienoic acid ((*S*)-(+)-1m)



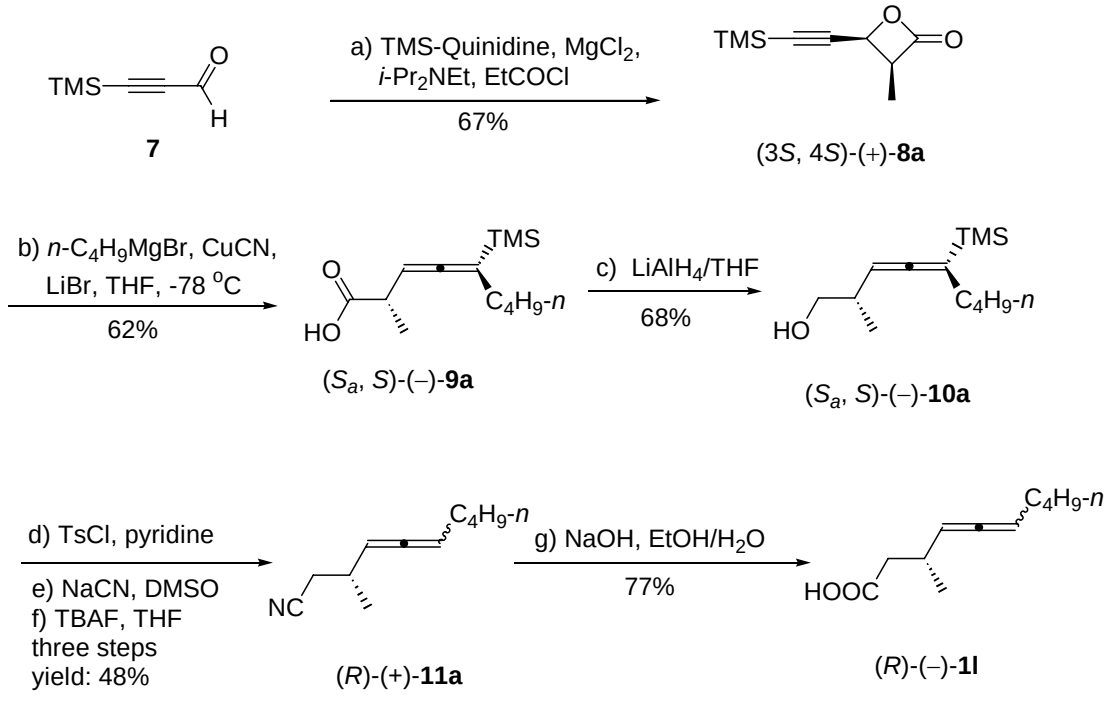
Following the procedure for the preparation of (*S*)-(–)-**11a**, the reaction of (*R*$_a$, *R*)-(–)-**10b** (0.8022g, 2.8 mmol) in anhydrous pyridine (20 mL) with *p*-TsCl (1.6518 g, 8.6 mmol) afforded the tosylate, which was used in the next step without further purification. A mixture of the tosylate prepared above and NaCN (0.1512 g, 3 mmol) in dry DMSO (30 mL) was stirred for 29.6 h, quenched with 30 mL of H_2O, extracted by diethyl ether (30 mL × 3), washed with water, brine, dried over Na_2SO_4, filtrated, and concentrated in vacuum to afford the nitrile, which was used without further purification. The reaction of the nitrile prepared above and a solution of tetrabutylammonium fluoride in THF (2.5 mL, 1M) in 10 mL of anhydrous tetrahydrofuran afforded (*S*)-**11b** (0.4053 g). The product was used in the next step without further purification. Following the procedure for the preparation of **1a**, the reaction of (*S*)-**11b** (0.4053 g, 1.9 mmol), ethanol (8 mL), and NaOH solution (2.0 g in 2.5 mL of H_2O, 50 mmol) afforded (*S*)-(+)-**1m** (0.1134 g, the combined yield from (*R*$_a$, *R*)-(–)-**10b** to (*S*)-(+)-**1m** is 17%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.04 (bs, COOH, 1H), 5.19-5.11 (m, 1H), 5.11-5.03 (m, 1H), 2.61-2.48 (m, 1H), 2.41-2.36 (m, 2H), 2.03-1.89 (m, 2H), 1.46-1.16 (m, 12H), 0.96-0.80 (m, 6H); $[\alpha]^{20}_D$ = +1.7 (*c* = 0.98, $CHCl_3$). The *dr* value of (*S*)-(+)-**1m** was determined after its conversion to the corresponding methyl ester.

(e) Synthesis of methyl (*S*)-3-propyldodeca-4,5-dienoate ((S)-(−)-13m)

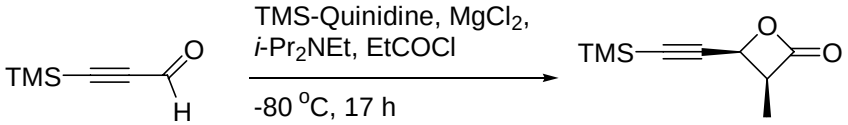


To a solution of (*S*)-3-propyldodeca-4,5-dienoic acid ((*S*)-(+)-**1m**) (14.1 mg, 0.06 mmol) in 1 mL of DMF was added K_2CO_3 (17.1 mg, 0.12 mmol) and MeI (13.5 mg, 0.09 mmol) sequentially. The resulting mixture was then stirred at 30 °C for 6.3 h as monitored by TLC, quenched with 10 mL of H2O, extracted by ether, washed with water and brine, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the crude product was purified by flash column chromatography on silica gel afforded (S)-(–)-**13m** (14.9 mg, 100%), the *dr* value was determined by GC to be 1.7/1 (GC condition: Column: HP-INNOWAX; carrier: N_2, 10.0 psi; injector: 250 °C; Detector: 250 °C; Oven temperature: 50 °C (2 min), 5 °C/min to 180 °C (10 min); t_R 31.4 (major), 31.6 (minor)). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.18-5.08 (m, 1H), 5.08-4.99 (m, 1H), 3.66 (s, 3H), 2.60-2.45 (m, 1H), 2.37-2.30 (m, 2H), 2.02-1.89 (m, 2H), 1.44-1.19 (m, 12H), 0.94-1.83 (m, 6H); IR (neat) ν = 1962, 1743, 1458, 1436, 1361, 1259, 1164 cm^{-1}; MS (70 ev, EI) *m/z* (%) 252 (M^+, 35.9), 79 (100); HRMS Calcd for $C_{16}H_{28}O_2Na$ (M^++Na): 275.1982, Found: 275.1981. $[\alpha]^{20}_D$ = -3.6 (*c* = 0.69, $CHCl_3$).

(5) Preparation of (*R*)-3-methyldeca-4,5-dienoic acid ((*R*)-(–)-1l)



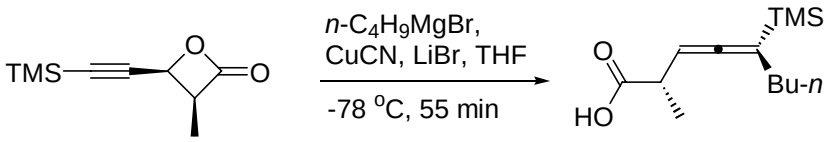
(a) Synthesis of (3*S*, 4*S*)-(+)-3-methyl-4-(trimethylsilyl)ethynyloxetan-2-one ((3*S*, 4*S*)-(+)-8a)[4]



7 (3*S*, 4*S*)-(+)-**8a**

Following the procedure for the preparation of (3*R*, 4*R*)-(–)-**8a**, the reaction of $MgCl_2$ (2.0533 g, 22 mmol), anhydrous diethyl ether (20 mL), *N*,*N*-diisopropylethylamine (7.0148 g, 55 mmol), *O*-trimethylsilylquinidine (0.9285 g, 2.2 mmol), 60 mL of anhydrous CH_2Cl_2, **7**[5] (2.7909 g, 22 mmol) in anhydrous CH_2Cl_2 (5 mL), and propionyl chloride (4.1710 g, 44 mmol) in anhydrous CH_2Cl_2 (5 mL) afforded (3*S*, 4*S*)-(+)-**8a** (2.7548 g, 67%): liquid, the ^{1}H NMR date are the same as those for (3*R*, 4*R*)-(–)-**8a**. $[\alpha]^{20}_D$ = +14.0 (*c* = 3.07, $CHCl_3$).

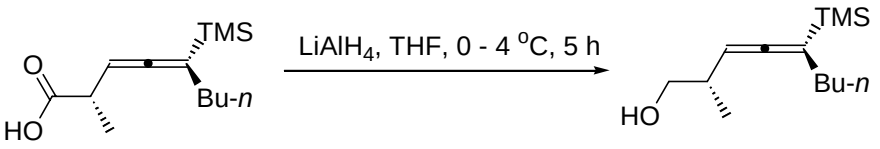
(b) Synthesis of (*S*$_a$, *S*)-(–)-2-methyl-5-(trimethylsilyl)nona-3,4-dienoic acid ((*S*$_a$, *S*)-(–)-9a)



(3*S*, 4*S*)-(+)-**8a** (*S*$_a$, *S*)-(–)-9**a**

Following the procedure for the preparation of (*R*$_a$, *R*)-(+)-**9a**, the reaction of a solution of C_4H_9MgBr in anhydrous THF (42 mL, 1 M, 42 mmol), (3*S*, 4*S*)-(+)-**8b** (2.5391 g, 14 mmol), CuCN (127.9 mg, 0.14 mmol), and anhydrous lithium bromide (0.2785 mg, 3.16 mmol) in THF (80 mL) afforded (*S*$_a$, *S*)-(–)-**9a** (2.0637 g, 62 %): liquid, the ^{1}H NMR date are the same as those for (*R*$_a$, *R*)-(+)-**9a**. $[\alpha]^{20}_D$ = -29.9 (*c* = 1.14, $CHCl_3$). This compound was used in the next step without further characterization.

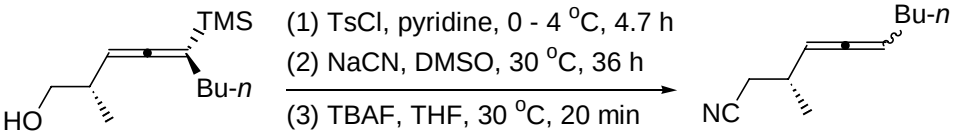
(c) Synthesis of (*S*$_a$, *S*)-(+)-2-methyl-5-(trimethylsilyl)nona-3,4-dien-1-ol ((*S*$_a$, *S*)-(+)-10a)



(S_a, *S*)-(–)-**9a** (S_a, *S*)-(+)-**10a**

Following the procedure for the preparation of (*R*)-**5a,** a solution of (S_a, *S*)-(–)-**9a** (1.9222 g, 8.0 mmol) in anhydrous ether (10 mL) was added to a suspension of $LiAlH_4$ (0.3657 g, 9.6 mmol) in anhydrous ether (60 mL) to afford (S_a, *S*)-(+)-**10a** (1.2308 g, 68%): liquid, the ^1H NMR date are the same as those for (R_a, *R*)-(–)-**10a**. $[\alpha]^{20}_D$ = +1.5 (*c* = 1.47, $CHCl_3$). This compound was used in the next step without further characterization.

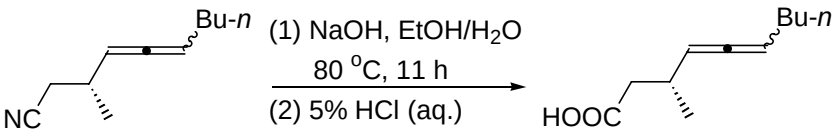
(d) Synthesis of (*R*)-(+)-3-methyldeca-4,5-dienenitrile ((*R*)-(+)-11a)



(S_a, *S*)-(+)-**10a** (*R*)-(+)-**11a**

Following the procedure for the preparation of (*R*)-**6b**, a mixture of (S_a, *S*)-(+)-**10a** (1.2008 g, 5.3 mmol) and pyridine (dried over Na_2SO_4, 10 mL) was treated with *p*-TsCl (3.3204, 15.9 mmol) to afford the tosylate, which was used in the next step without further purification. The reaction of the tosylate prepared above and NaCN (0.2901 g, 5.7 mmol) in anhydrous DMSO (10 mL) afforded (S_a, *R*)-3-methyl-6-trimethylsilyldeca-4,5-dienenitrile, which was used in the next step without further purification. The reaction of the nitrile prepared above and a solution of tetrabutylammonium fluoride in THF (4 mL, 1M, 4 mmol) in 10 mL of anhydrous tetrahydrofuran afforded (*R*)-(+)-**11a** (0.3763 mg, the combined yield from (S_a, *S*)-(+)-**10a** to (*R*)-(+)-**11a** is 43%): liquid, the ^1H NMR date are the same as those for (*S*)-(–)-**11a**. $[\alpha]^{20}_D$ = +14.0 (*c* = 1.13, $CHCl_3$). This compound was used in the next step without further characterization.

(e) Synthesis of (*R*)-(–)-3-methyldeca-4,5-dienoic acid ((*R*)-(–)-1l)

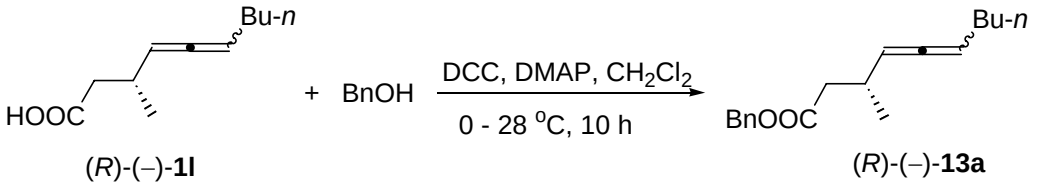


(*R*)-(+)-**11a** (*R*)-(–)-**1l**

Following the procedure for the preparation of **6a**, the reaction of (*R*)-(+)-**11a** (0.3456 g, 2.1 mmol), ethanol (8 mL), and NaOH solution (2.0014 g in 2.5 mL of H_2O, 50 mmol) afforded (*R*)-(–)-**1l** (0.2988 g, 77%, *dr* = 1.2/1): liquid, the ^{1}H NMR date are the same as those for (*S*)-(+)-**1l**. $[\alpha]^{20}_D$ = -12.5 (*c* = 1.24, $CHCl_3$).

The *dr* value of (*R*)-(–)-**1l** was determined after its conversion to the corresponding benzyl ester.

(f) Synthesis of benzyl (*R*)-(–)-3-methyldeca-4,5-dienoate ((*R*)-(–)-13a)



(*R*)-(–)-**1l** (*R*)-(–)-**13a**

Following the procedure for the preparation of (R_a, *R*)-(–)-**13a**, the reaction of (*R*)-(–)-**1l** (52.8 mg, 0.29 mmol), BnOH (92.5 mg, 0.86 mmol), DMAP (27.5 mg, 0.23 mmol), and DCC (65.1 mg, 0.32 mmol) in CH_2Cl_2 (1.8 mL) afforded (*R*)-(–)-**13a** (69.9 mg, 89%, *dr* = 1.2/1, (HPLC conditions: Chiralcel OJ-H column; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 99/1; λ = 214 nm, t_R 9.4 (minor), 9.9 (major)): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.29 (m, 5H), 5.20-5.06 (m, 4H), 2.74-2.61 (m, 1H), 2.52-2.39 (m, 1H), 2.36-2.22 (m, 1H), 2.01-1.88 (m, 2H), 1.42-1.26 (m, 4H), 1.08-1.02 (m, 3H), 0.92-0.84 (m, 3H); IR (neat) ν = 1961, 1740, 1498, 1456, 1377, 1261, 1155 cm^{-1}; MS (70 ev, EI) *m/z* (%) 272 (M^+, 0.57), 139 (100); HRMS Calcd for $C_{18}H_{24}O_2Na$ (M^++Na): 295.1669, Found: 295.1666. $[\alpha]^{20}_D$ = -5.6 (*c* = 0.33, $CHCl_3$).

(g) Preparation of (S_a, *R*)-(+)-3-methyldeca-4,5-dienoic acid ((S_a, *R*)-(+)-1l)

The two isomers (S_a, *R*)-(+)-**13a** and (R_a, *R*)-(–)-**13a** were separated by using CHIRALPAK IC column (25 cm × 2 cm); rate, 9 mL/min; eluent, hexane/ethyl acetate = 98/2; λ = 214 nm, injection, 2 mL (C = 1 mg/mL): Peak 1, t_R = 13.7, Peak 2 t_R = 15.0. The two portions collected was kept over dry ice. After evaporation of the solvent, pure isomers were obtained.

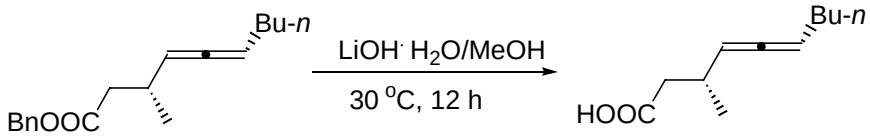
(S_a, *R*)-(+)-**13a**: Peak No. 1: *dr* > 99/1 (HPLC conditions: Chiralcel OJ-H column; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 99/1; λ = 214 nm, t_R 9.377 (major, (S_a, *R*)-(+)-**13a**), t_R 9.930 (minor, (R_a, *R*)-(–)-**13a**)): liquid, ^{1}H NMR (300 MHz, $CDCl_3$)

δ 7.42-7.29 (m, 5H), 5.20-5.06 (m, 4H), 2.76-2.63 (m, 1H), 2.46 (dd, J_1 = 15.2 Hz, J_2 = 6.8 Hz, 1H), 2.30 (dd, J_1 = 15.2 Hz, J_2 = 7.4 Hz, 1H), 2.01-1.89 (m, 2H), 1.41-1.27 (m, 4H), 1.05 (d, J = 6.9 Hz, 3H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.4, 172.4, 136.0, 128.5, 128.17, 128.15, 95.7, 93.2, 66.1, 41.4, 31.3, 30.0, 28.6, 22.2, 20.2, 13.9; IR (neat) ν = 1962, 1737, 1499, 1456, 1161 cm^{-1}; MS (70 ev, EI) *m/z* (%) 272 (M^+, 0.58), 91 (100); HRMS Calcd for $C_{18}H_{24}O_2$ (M^+): 272.1776, Found: 272.1778. $[\alpha]^{20}_D$ = +42 (*c* = 0.80, $CHCl_3$).

(R_a, *R*)-(–)-**13a**: Peak No. 2: *dr* > 98/2, (HPLC conditions: Chiralcel OJ-H column; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 99/1; λ = 214 nm, t_R 9.377 (minor, (S_a, *R*)-(+)-**13a**), t_R 9.930 (major, (R_a, *R*)-(–)-**13a**)): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.28 (m, 5H), 5.20-5.06 (m, 4H), 2.76-2.63 (m, 1H), 2.46 (dd, J_1 = 15.3 Hz, J_2 = 6.9 Hz, 1H), 2.29 (dd, J_1 = 15.2 Hz, J_2 = 7.7 Hz, 1H), 2.01-1.89 (m, 2H), 1.41-1.27 (m, 4H), 1.05 (d, J = 6.9 Hz, 3H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.4, 172.5, 136.0, 128.5, 128.2, 128.16, 95.7, 93.3, 66.1, 41.3, 31.3, 30.0, 28.6, 22.2, 20.3, 13.9; IR (neat) ν = 1961, 1737, 1498, 1456, 1379, 1351, 1263, 1161 cm^{-1}; MS (70 ev, EI) *m/z* (%) 272 (M^+, 0.54), 141 (100); HRMS Calcd for $C_{18}H_{24}O_2$ (M^+): 272.1776, Found: 272.1775. $[\alpha]^{20}_D$ = -50 (*c* = 0.50, $CHCl_3$).

The absolute configuration of the isomer related to Peak No. 2 was determined as (R_a, *R*) by the comparison with the specific optical rotation of (R_a, *R*)-(–)-**13a** prepared on Page S47. The absolute configuration of the isomer related to Peak No. 1 was then assigned as (S_a, *R*).

(h) Synthesis of (S_a, *R*)-(+)-3-methyldeca-4,5-dienoic acid ((S_a, *R*)-(+)-1l)



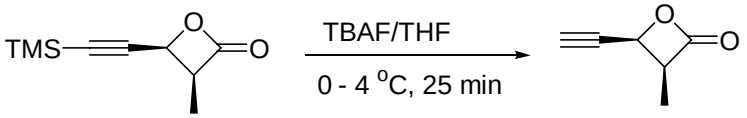
(S_a, *R*)-(+)-**13a** (S_a, *R*)-(+)-**1l**

To a solution of (S_a, *R*)-(+)-**13a** (16 mg, 0.06 mmol) prepared above in 0.3 mL of H_2O and 0.6 mL of MeOH was added LiOH•H_2O (8 mg, 0.18 mmol). After being stirred for 12 h at 30 °C, the reaction was complete as monitored by TLC (eluent: petroleum ether/ethyl acetate = 5/1), adjusted with 5% HCl (aq.) to pH = 1, and

extracted with ether (30 mL × 3). The ether layer was then washed subsequently with water and brine, dried over Na_2SO_4, filtrated, and concentrated under vacuum. Chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) of the crude product afforded (S_a, *R*)-(+)-**1l** (7.1 mg, 66%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.21-5.09 (m, 2H), 2.73-2.58 (m, 1H), 2.45 (dd, J_1 = 15.6 Hz, J_2 = 6.9 Hz, 1H), 2.29 (dd, J_1 = 15.6 Hz, J_2 = 7.2 Hz, 1H), 2.05-1.90 (m, 2H), 1.46-1.24 (m, 4H), 1.08 (d, *J* = 6.9 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H); The acidic proton is missing here in this spectrum. ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.4, 178.7, 95.6, 93.5, 41.0, 31.3, 29.7, 28.6, 22.2, 20.2, 13.9; IR (neat) ν = 1962, 1710, 1458, 1410, 1378, 1293 cm^{-1}; MS (70 ev, EI) *m/z* (%) 182 (M^+, 3.54), 81 (100); HRMS Calcd for $C_{11}H_{18}O_2$ (M^+): 182.1307, Found: 182.1308. $[\alpha]^{20}_D$ = +45 (*c* = 1.00, $CHCl_3$).

(6) Preparation of (R_a, *R*)-(–)-3-methyldeca-4,5-dienoic acid ((R_a, *R*)-(–)-1l)

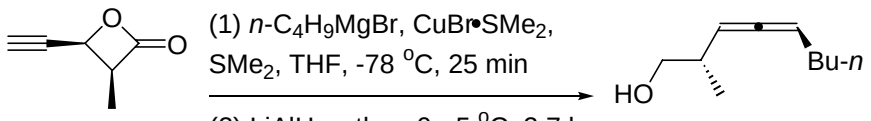
(a) Synthesis of (3*S*, 4*S*)-(–)-3-methyl-4-ethynyloxetan-2-one ((3*S*, 4*S*)-(–)-12a)[8]



(3*S*, 4*S*)-(+)-**8a** (3*S*, 4*S*)-(–)-**12a**

To a solution of (3*S*, 4*S*)-(+)-**8a** (2.3543 g, 13 mmol) in 20 mL of anhydrous tetrahydrofuran was added a solution of tetrabutylammonium fluoride in THF (14.0 mL, 1 M, 14 mmol). The mixture was stirred at 0 °C for 25 min, the resulting mixture was filtrated through a 1.5 cm plug of silica gel, eluting with CH_2Cl_2. The filtrate was concentrated and purified by flash chromatography on silica gel (petroleum ether(30 - 60 °C)/ ether = 5/1) to afford (3*S*, 4*S*)-(–)-**12a** (0.7234 g, 51%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.13 (dd, J_1 = 6.6 Hz, J_2 = 2.1 Hz, 1H), 3.95-3.85 (m, 1H), 2.84 (d, *J* = 2.1 Hz, 1H), 2.44 (d, *J* = 7.8 Hz, 3H). $[\alpha]^{20}_D$ = -5.4 (*c* = 0.70, $CHCl_3$).

(b) Synthesis of (R_a, *S*)-(–)-2-methylnona-3,4-dien-1-ol ((R_a, *S*)-(–)-10a)

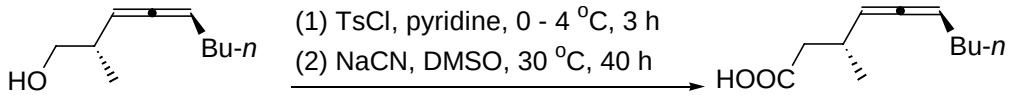


(3*S*,4*S*)-(–)-**12a** (R_a, *S*)-(–)-**10a**

To a solution of CuBr•SMe_2 (6.8 mg, 0.03 mmol) and dimethylsulfide (0.2 mL) in

3.5 mL of anhydrous THF, was added (3*S*, 4*S*)-(–)-**12a** (34.1 g, 0.3 mmol). Then the Grignard reagent solution (0.65 mL, 1M in THF, 0.65 mmol) was added dropwise to the mixture at –78 ^{o}C within 5 min. After being stirred at –78 °C for additional 20 min, the reaction was quenched with a saturated aqueous NH_4Cl solution (10 mL). The resulting mixture was extracted with ether (30 mL × 3) and the combined organic extracts were successively washed with H_2O and brine, dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash chromatography on silica gel to afford (R_a, *S*)-2-methylnona-3,4-dienoic acid as a colorless oil (0.0415 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.78 (br, 1H), 5.35-5.20 (m, 2H), 3.21-3.04 (m, 1H), 2.09-1.90 (m, 2H), 1.44-1.31 (m, 4H), 1.27 (d, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). $[\alpha]^{20}_D$ = -110.9 (*c* = 1.21, $CHCl_3$). It was used in the next step without further purification. Following the procedure for the preparation of (*R*)-(–)-**5a,** a solution of the dienoic acid prepared above (0.3229 g, 1.9 mmol) in anhydrous ether (3 mL) was added to a suspension of $LiAlH_4$ (0.1441 g, 3.8 mmol) in anhydrous ether (15 mL) to afford (R_a, *S*)-(–)-**10a** (0.1284 g, 43%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.21-5.11 (m, 1H), 5.10-5.01 (m, 1H), 3.48 (d, *J* = 6.3 Hz, 2H), 2.39-2.28 (m, 1H), 2.03-1.92 (m, 2H), 1.91 (br, 1H), 1.43-1.24 (m, 4H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H). $[\alpha]^{20}_D$ = -82.3 (*c* = 0.39, $CHCl_3$). This compound was used in the next step without further characterization.

(c) Synthesis of (R_a, *R*)-(–)-3-methyldeca-4,5-dienoic acid ((R_a, *R*)-(–)-1l)

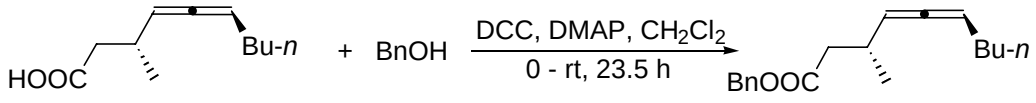


(R_a, *S*)-(–)-**10a** (R_a, *R*)-(–)-**1l**

Following the procedure for the preparation of (*R*)-(–)-**6a**, a mixture of (R_a, *S*)-(–)-**10a** (0.1284 g, 0.8 mmol) and anhydrous pyridine (1 mL) was treated with *p*-TsCl (0.4785 g, 2.5 mmol) to afford the tosylate, which was used in the next step without further purification. The reaction of the tosylate prepared above and NaCN (0.0482 g, 0.96 mmol) in anhydrous DMSO (2 mL) afforded (R_a, *S*)-3-methyldeca-4,5-dienenitrile, which was used in the next step without further purification. Following the procedure for the preparation of **6a**, the reaction of (R_a,

S)-3-methyldeca-4,5-dienenitrile (0.0814 g, 0.5 mmol), ethanol (2 mL), and NaOH solution (0.4 g in 0.6 mL of H_2O, 10 mmol) afforded (R_a, *R*)-(–)-**1l** (0.0660 g, the combined yield from (R_a, *S*)-(–)-**10a** to (R_a, *R*)-(–)-**1l** is 43%): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.65 (bs, COOH, 1H), 5.21-5.09 (m, 2H), 2.73-2.60 (m, 1H), 2.44 (dd, J_1 = 15.6 Hz, J_2 = 7.0 Hz, 1H), 2.23 (dd, J_1 = 15.6 Hz, J_2 = 7.3 Hz, 1H), 2.05-1.90 (m, 2H), 1.46-1.24 (m, 4H), 1.08 (d, *J* = 6.6 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.4, 179.3, 95.5, 93.4, 41.2, 31.3, 29.8, 28.6, 22.2, 20.3, 13.9; IR (neat) ν = 1962, 1710, 1458, 1410, 1378, 1294 cm^{-1}; MS (70 ev, EI) *m/z* (%) 182 (M^+, 1.90), 140 (100); HRMS Calcd for $C_{11}H_{18}O_2$ (M^+): 182.1307, Found: 182.1307. $[\alpha]^{20}_D$ = -74.9 (*c* = 1.34, $CHCl_3$).

(d) Synthesis of benzyl (R_a, *R*)-(–)-3-methyldeca-4,5-dienoate ((R_a, *R*)-(–)-13a)

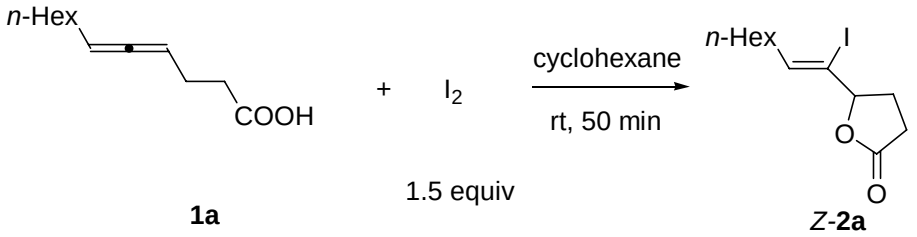


(R_a, *R*)-(–)-**1l** (R_a, *R*)-(–)-**13a**

To a solution of (R_a, *R*)-(–)-**1l** (8.9 mg, 0.055 mmol) in CH_2Cl_2 (1 mL) were added BnOH (16.9 mg, 0.165 mmol) and DMAP (5.4 mg, 0.044 mmol) sequentially. Then DCC (13.6 mg, 0.06 mmol) was added at 0 °C. After being stirred for 23.5 h at rt, the reaction was over as monitored by TLC and the resulting mixture was diluted with 10 mL of ether and transferred to a round-bottomed flask and evaporated. The residue was purified by chromatography on silica gel to afford (R_a, *R*)-(–)-**13a** (13.3 mg, 100%, *dr* = 96/4, HPLC conditions: Chiralcel OJ-H column; rate, 0.5 mL/min; eluent, hexane/*i*-PrOH = 99/1; λ = 214 nm, t_R 12.1 (minor), 12.5 (major)): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.29 (m, 5H), 5.20-5.06 (m, 4H), 2.76-2.62 (m, 1H), 2.47 (dd, J_1 = 15.4 Hz, J_2 = 6.9 Hz, 1H), 2.30 (dd, J_1 = 15.4 Hz, J_2 = 7.7 Hz, 1H), 2.02-1.89 (m, 2H), 1.40-1.29 (m, 4H), 1.06 (d, *J* = 6.9 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H); $[\alpha]^{20}_D$ = -54.9 (*c* = 0.36, $CHCl_3$).

Procedure for the preparation of 4,5-dihydro-2(3*H*)-furanones (*Z*-2a-m)

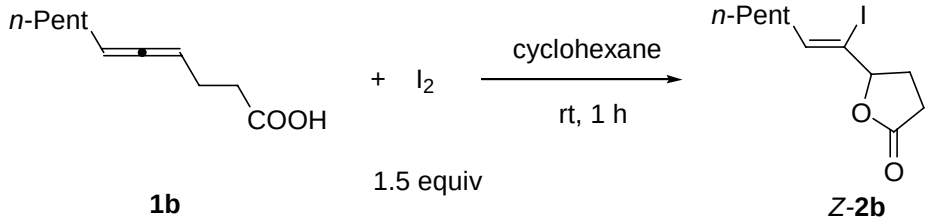
(1) 5-(1'-Iodo-1'(*Z*)-octenyl)-4,5-dihydro-2(3*H*)-furanone (*Z*-2a). Typical Procedure.



1a *Z*-**2a**

To a solution of **1a** (59.3 mg, 0.3 mmol) in cyclohexane (4 mL) was added I_2 (114.3 mg, 0.45 mmol, solid) with stirring at rt. After the reaction was complete as monitored by TLC (eluent: petroleum ether/ethyl acetate = 5/1), it was quenched with H_2O (6 mL), which was followed by the addition of sat. aqueous $Na_2S_2O_3$ (4 mL). The resulting mixture was extracted with ether (20 mL × 3), washed with brine, dried over Na_2SO_4, and filtrated. After evaporation of the solvent, the *Z/E* ratio of products was determined to be 98/2 by 400 MHz ^{1}H NMR analysis. Chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) of the crude product afforded *Z*-**2a** (81 mg, 83%, *Z/E* = 98/2): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (td, J_1 = 6.6 Hz, J_2 = 1 Hz, 1H), 4.76 (t, *J* = 7.0 Hz, 1H), 2.70-2.58 (m, 1H), 2.58-2.45 (m, 1H), 2.45-2.33 (m, 1H), 2.21-2.08 (m, 3H), 1.45-1.34 (m, 2H), 1.34-1.16 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 138.5, 106.9, 84.3, 35.5, 31.5, 28.8, 28.6, 28.0, 27.9, 22.5, 14.0; IR (neat) ν = 2955, 2926 , 2855, 1785, 1640, 1457, 1316, 1180, 1024 cm^{-1}; MS (70 ev, EI) *m/z* (%) 322 (M^+, 30.18), 111 (100); Anal. Cacld for $C_{12}H_{19}IO_2$: C, 44.74; H, 5.94; Found: C, 44.74; H, 6.01.

(2) 5-(1'-Iodo-1'(*Z*)-heptenyl)-4,5-dihydro-2(3*H*)-furanone (*Z*-2b)

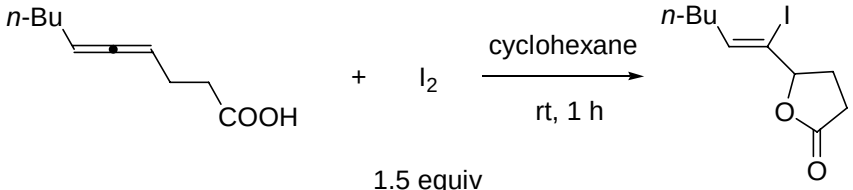


1b *Z*-**2b**

The reaction of **1b** (53.6 mg, 0.3 mmol) in cyclohexane (4 mL) with I_2 (115.3 mg, 0.45 mmol) afforded *Z*-**2b** (76.8 mg, 85%, *Z/E* = 98/2): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.03 (t, *J* = 6.8 Hz, 1H), 4.77 (t, *J* = 6.9 Hz, 1H), 2.71-2.32 (m, 3H), 2.26-2.07 (m, 3H), 1.50-1.35 (m, 2H), 1.35-1.18 (m, 4H), 0.87 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 138.5, 106.9, 84.3, 35.4, 31.2, 28.6, 28.0, 27.6, 22.4, 13.9; IR (neat) ν = 2956, 2927, 2857, 1785, 1639, 1456, 1419, 1317, 1261, 1180,

1020 cm^{-1}; MS (70 ev, EI) *m/z* (%) 308 (M^+, 73.81), 111 (100); HRMS Calcd for $C_{11}H_{17}IO_2$ (M^+): 308.0268, Found: 308.0266.

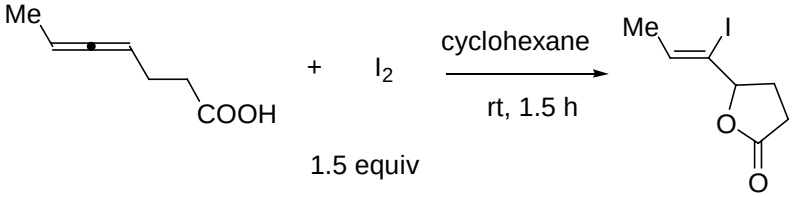
(3) 5-(1'-Iodo-1'(*Z*)-hexenyl)-4,5-dihydro-2(3*H*)-furanone (*Z*-2c)



1c *Z*-**2c**

The reaction of **1c** (50.4 mg, 0.3 mmol) in cyclohexane (4 mL) with I_2 (114.7 mg, 0.45 mmol) afforded *Z*-**2c** (74.8 mg, 85%, *Z/E* = 97/3): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (td, J_1 = 6.8 Hz, J_2 = 0.7 Hz, 1H), 4.77 (t, *J* = 6.8 Hz, 1H), 2.70-2.59 (m, 1H), 2.59-2.46 (m, 1H), 2.46-2.34 (m, 1H), 2.23-2.08 (m, 3H), 1.44-1.26 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 138.5, 106.9, 84.2, 35.2, 30.0, 28.6, 28.0, 22.1, 13.8; IR (neat) ν = 2957, 2928, 2871, 2858, 1775, 1645, 1456, 1418, 1378, 1316, 1181, 1133, 1032, 1014 cm^{-1}; MS (70 ev, EI) *m/z* (%) 294 (M^+, 94.10), 111 (100); HRMS Calcd for $C_{10}H_{15}IO_2$ (M^+): 294.0111, Found: 294.0124.

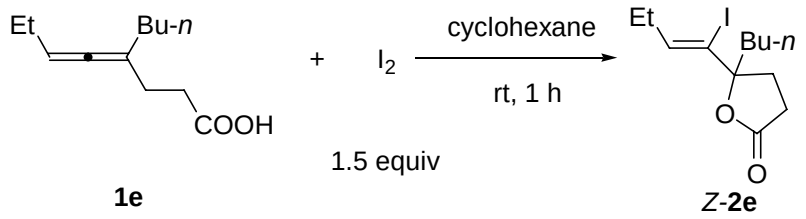
(4) 5-(1'-Iodo-1'(*Z*)-propenyl)-4,5-dihydro-2(3*H*)-furanone (*Z*-2d)



1d *Z*-**2d**

The reaction of **1d** (38.7 mg, 0.3 mmol) in cyclohexane (4 mL) with I_2 (115.7 mg, 0.45 mmol) afforded *Z*-**2d** (61.1 mg, 79%, *Z/E* = 98/2): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (q, *J* = 6.4 Hz, 1H), 4.78 (t, *J* = 7.0 Hz, 1H), 2.70-2.60 (m, 1H), 2.60-2.46 (m, 1H), 2.45-2.36 (m, 1H), 2.22-2.16 (m, 1H), 1.81 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 133.4, 108.7, 84.2, 28.5, 28.0, 21.3; IR (neat) ν = 2956, 2923, 2852, 1774, 1642, 1458, 1377, 1261, 1179, 1021 cm^{-1}; MS (70 ev, EI) *m/z* (%) 252 (M^+, 69.05), 125 (100); HRMS Calcd for $C_7H_9IO_2$ (M^+): 251.9642, Found: 251.9653 .

(5) 5-Butyl-5-(1'-Iodo-1'(*Z*)-butenyl)-4,5-dihydro-2(3*H*)-furanone (*Z*-2e)

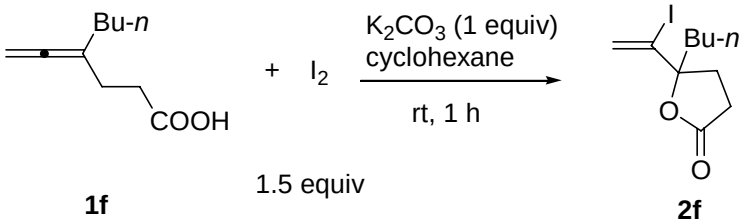


1e *Z*-**2e**

The reaction of **1e** (56.3 mg, 0.3 mmol) in cyclohexane (4 mL) with I_2 (114.2 mg, 0.45 mmol) afforded *Z*-**2e** (69.8 mg, 75%, *Z*/*E* = 99/1): liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 (t, *J* = 6.6 Hz, 1H), 2.55-2.43 (m, 3H), 2.23-1.98 (m, 4H), 1.74-1.61 (m, 1H), 1.34-1.14 (m, 4H), 0.99 (t, *J* = 7.5 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 137.4, 108.2, 90.2, 39.0, 33.8, 29.9, 28.0, 25.4, 22.5, 13.8, 12.7; IR (neat) ν = 2959, 2932, 2872, 1785, 1630, 1458, 1378, 1265, 1183, 1116, 1025 cm^{-1}; MS (70 ev, EI) *m/z* (%) 322 (M^+, 14.47), 265 (100); HRMS Calcd for $C_{12}H_{19}IO_2$ (M^+): 322.0424, Found: 322.0421.

Iodocyclization of 1f-h in the presence of I_2 and K_2CO_3

(1) 5-Butyl-5-(1'-iodo-1'-vinyl)-4,5-dihydro-2(3*H*)-furanone (2f). Typical Procedure.

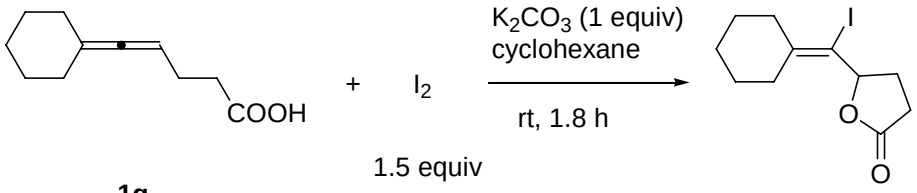


1f **2f**

To a solution of **1f** (50.5 mg, 0.3 mmol) in cyclohexane (4 mL) was added K_2CO_3 (43.7 mg, 0.3 mmol). After stirring for 20 min, I_2 (116.0 mg, 0.45 mmol, solid) was added, which was followed by stirring for 1 h. The resulting mixture was quenched sequentially with H_2O (6 mL) and sat. aqueous $Na_2S_2O_3$ (4 mL), extracted with ether (25 mL × 3), washed with brine, dried over Na_2SO_4, and filtrated. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to afford **2f** (76.9 mg, 87%): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 (d, *J* = 2.2 Hz, 1H), 5.91 (d, *J* = 2.2 Hz, 1H), 2.55-2.43 (m, 3H), 2.14-2.01 (m, 2H), 1.73-1.64 (m, 1H), 1.42-1.20 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 126.9, 111.4, 90.2, 38.6, 33.2, 28.1, 25.5, 22.5, 13.8; IR (neat) ν = 2956, 2930, 2871, 1784, 1611, 1456, 1183, 1090, 1024 cm^{-1}; MS (70 ev,

EI) *m/z* (%) 294 (M^+, 0.36), 237 (M^+-C_4H_9, 100); HRMS Calcd for $C_{10}H_{15}IO_2$ (M^+): 294.0111, Found: 294.0130.

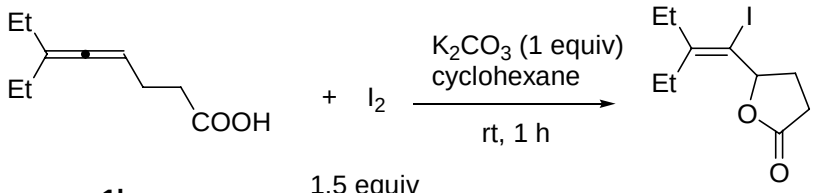
(2) 5-(2,2-Pentamethyleneiodovinyl)-4,5-dihydro-2(3*H*)-furanone (2g)



1g **2g**

The reaction of **1g** (53.5 mg, 0.3 mmol) in cyclohexane (4 mL) with K_2CO_3 (42.8 mg, 0.3 mmol) and I_2 (115.8 mg, 0.45 mmol) afforded **2g** (66.6 mg, 73%): solid, M.p 79-80 ^oC (*n*-hexane/diethyl ether), ^1H NMR (400 MHz, $CDCl_3$) δ 5.13 (t, J = 7.4 Hz, 1H), 2.72 (ddd, J_1 = 18.0 Hz, J_2 = 10.6 Hz, J_3 = 4.6 Hz, 1H), 2.61-2.37 (m, 5H), 2.37-2.22 (m, 1H), 2.20-2.07 (m, 1H), 1.68-1.40 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 150.0, 101.8, 78.1, 42.6, 32.7, 29.0, 28.6, 28.2, 27.4, 26.4; IR (KBr) ν = 2929, 2854, 1756, 1618, 1446, 1319, 1296, 1224, 1184, 1148, 1024 cm^{-1}; MS (70 ev, EI) *m/z* (%) 306 (M^+, 22.04), 137(100); Anal. Cacld for: $C_{11}H_{15}IO_2$ (%) C, 43.16; H, 4.94; Found: C, 43.17; H, 5.02.

(3) 5-(2'-Ethyl-1'-iodo-1'-butenyl)-4,5-dihydro-2(3*H*)-furanone (2h)

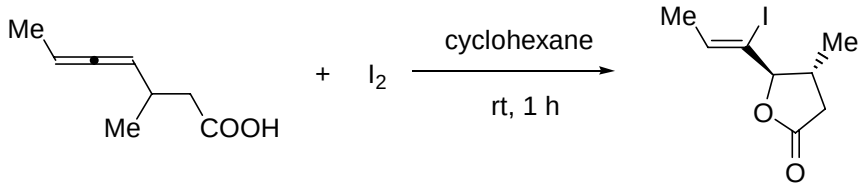


1h **2h**

The reaction of **1h** (49.2 mg, 0.3 mmol) in cyclohexane (4 mL) with K_2CO_3 (41.4 mg, 0.3 mmol) and I_2 (114.1 mg, 0.45 mmol) afforded **2h** (78 mg, 88%): liquid, ^1H NMR (400 MHz, $CDCl_3$) δ 4.98 (t, J = 7.2 Hz, 1H), 2.70 (ddd, J_1 = 18.0 Hz, J_2 = 10.6 Hz, J_3 = 4.6 Hz, 1H), 2.61-2.48 (m, 1H), 2.40-2.21 (m, 5H), 2.19-2.06 (m, 1H), 1.06-0.92 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 153.2, 104.1, 78.5, 35.8, 28.9, 28.5, 26.0, 14.1, 11.5; IR (neat) ν = 2969, 2934, 2873, 1779, 1622, 1456, 1182, 1144, 1020 cm^{-1}; MS (70 ev, EI) *m/z* (%) 294 (M^+, 41.61), 125 (100); HRMS Calcd for $C_{10}H_{15}IO_2$ (M^+): 294.0111, Found: 294.0115.

Iodocyclization reaction of 3-substituded-4,5-allenoic acids 2i-m

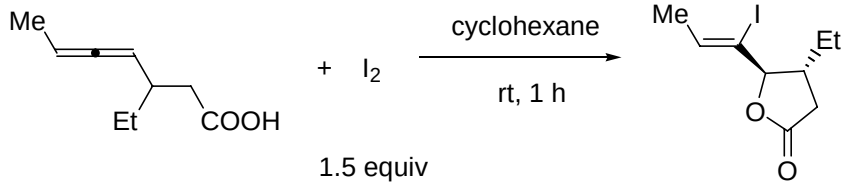
(1) *trans*-5-(1'-Iodo-1'(*Z*)-propenyl)-4-methyl-4,5-dihydro-2(3*H*)-furanone (*trans-Z*-2i)



1i 1.5 equiv *trans-Z*-**2i**

The reaction of **1i** (42.0 mg, 0.3 mmol) in cyclohexane (4 mL) with I_2 (115.6 mg, 0.45 mmol) afforded *trans-Z*-**2i** (65.9 mg, 82%, *Z/E* = 96/4): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (qd, J_1 = 6.4 Hz, J_2 = 0.8 Hz, 1H), 4.13 (d, J = 7.2 Hz, 1H), 2.77 (dd, J_1 = 17.4 Hz, J_2 = 8.6 Hz, 1H), 2.61-2.49 (m, 1H), 2.22 (dd, J_1 = 17.4 Hz, J_2 = 9.0 Hz, 1H), 1.83 (d, J = 6.0 Hz, 3H), 1.14 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 135.2, 107.9, 91.0, 36.3, 36.0, 21.4, 17.1; IR (neat) ν = 2964, 2917, 2875, 1785, 1642, 1457, 1420, 1381, 1365, 1342, 1316, 1286, 1267, 1208, 1169, 1130, 1090, 1000 cm^{-1}; MS (70 ev, EI) *m/z* (%) 266 (M^+, 60.24), 69 (100); HRMS Calcd for $C_8H_{11}IO_2$ (M^+): 265.9798, Found: 265.9803.

(2) *trans*-5-(1'-Iodo-1'(*Z*)-propenyl)-4-ethyl-4,5-dihydro-2(3*H*)-furanone (*trans-Z*-2j)



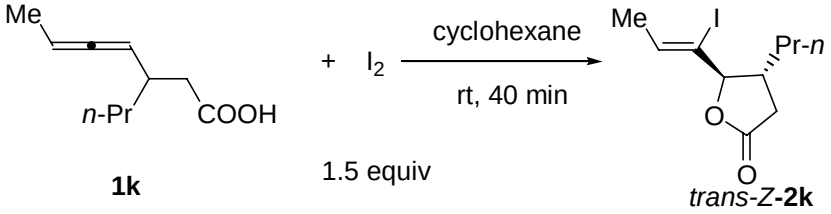
1.5 equiv

1j *trans-Z*-**2j**

The reaction of **1j** (46.4 mg, 0.3 mmol) in cyclohexane (4 mL) with I_2 (113.9 mg, 0.45 mmol) afforded *trans-Z*-**2j** (66 mg, 78%, *Z/E* = 97/3): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (q, J = 6.5 Hz, 1H), 4.25 (d, J = 6.8 Hz, 1H), 2.76 (dd, J_1 = 17.6 Hz, J_2 = 8.8 Hz, 1H), 2.45-2.34 (m, 1H), 2.22 (dd, J_1 = 17.6 Hz, J_2 = 8.0 Hz, 1H), 1.82 (d, J = 6.4 Hz, 3H), 1.66-1.54 (m, 1H), 1.48-1.35 (m, 1H), 0.94 (t, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.7, 134.8, 108.8, 89.5, 42.8, 33.9, 25.7, 21.5, 11.7; IR (neat) ν = 2960, 2925, 2875, 1783, 1642, 1460, 1261, 1202, 1167, 1032 cm^{-1}; MS (70 ev, EI) *m/z* (%) 280 (M^+, 79.53), 197 (100); HRMS Calcd for $C_9H_{13}IO_2$ (M^+):

279.9955, Found: 279.9960.

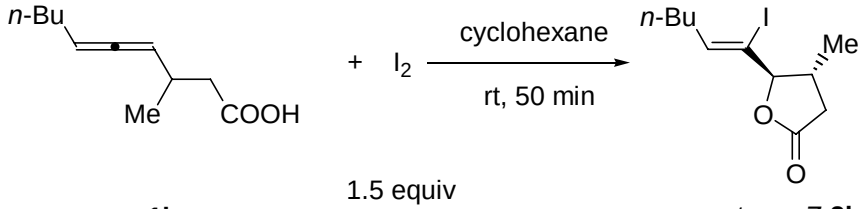
(3) *trans*-5-(1'-Iodo-1'(*Z*)-vinyl)-4-propyl-4,5-dihydro-2(3*H*)-furanone (*trans-Z*-2k)



1k *trans-Z*-**2k**

The reaction of **1k** (50.9 mg, 0.3 mmol) in cyclohexane (4 mL) with I_2 (114.0 mg, 0.45 mmol) afforded *trans-Z*-**2k** (73.1 mg, 82%, *Z/E* = 98/2): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (qd, J_1 = 6.4 Hz, J_2 = 0.8 Hz, 1H), 4.22 (d, J = 6.8 Hz, 1H), 2.75 (dd, J_1 = 17.6 Hz, J_2 = 8.8 Hz, 1H), 2.52-2.41 (m, 1H), 2.22 (dd, J_1 = 17.6 Hz, J_2 = 8.4 Hz, 1H), 1.82 (d, J = 6.4 Hz, 3H), 1.56-1.45 (m, 1H), 1.42-1.27 (m, 3H), 0.91 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 135.1, 108.8, 89.7, 41.1, 34.7, 34.3, 21.4, 20.5, 13.9; IR (neat) ν = 2958, 2928, 2872, 1785, 1640, 1262, 1224, 1198, 1166, 1131, 985 cm^{-1}; MS (70 ev, EI) *m/z* (%) 294 (M^+, 56.93), 197 (100); HRMS Calcd for $C_{10}H_{15}IO_2$ (M^+): 294.0111, Found: 294.0124.

(4) *trans*-5-(1'-Iodo-1'(*Z*)-hexenyl)-4-methyl-4,5-dihydro-2(3*H*)-furanone (*trans-Z*-2l)

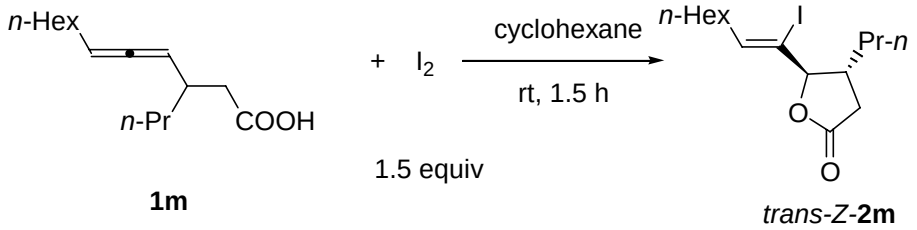


1l *trans-Z*-**2l**

The reaction of **1l** (54.0 mg, 0.3 mmol) in cyclohexane (4 mL) with I_2 (114.6 mg, 0.45 mmol) afforded *trans-Z*-**2l** (69.1 mg, 76%, *Z/E* = 97/3): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (t, J = 6.8 Hz, 1H), 4.12 (d, J = 7.2 Hz, 1H), 2.77 (dd, J_1 = 17.4 Hz, J_2 = 8.6 Hz, 1H), 2.62-2.50 (m, 1H), 2.28-2.14 (m, 3H), 1.46-1.28 (m, 4H), 1.15 (d, J = 6.8 Hz, 3H), 0.90 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 140.4, 106.1, 91.0, 36.3, 36.0, 35.3, 30.0, 22.2, 17.1, 13.8; IR (neat) ν = 2959, 2928, 2872, 2859, 1786, 1637, 1459, 1420, 1380, 1282, 1268, 1207, 1165, 1000 cm^{-1}; MS (70 ev, EI) *m/z* (%) 308 (M^+, 100); HRMS Calcd for $C_{11}H_{17}IO_2$ (M^+): 308.0268,

Found: 308.0280.

(5) *trans*-5-(1'(*Z*)-1'-Iodooctenyl)-4-propyl-4,5-dihydro-2(3*H*)-furanone (*trans*-*Z*-2m)

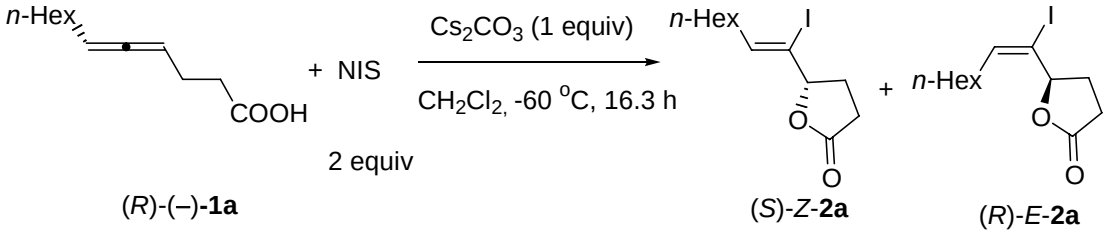


1m *trans*-*Z*-**2m**

The reaction of **1m** (72.7 mg, 0.3 mmol) in cyclohexane (4 mL) with I_2 (114.5 mg, 0.45 mmol) afforded *trans*-*Z*-**2m** (88.5 mg, 80%, *Z*/*E* = 97/3): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (t, *J* = 6.6 Hz, 1H), 4.21 (d, *J* = 6.4 Hz, 1H), 2.75 (dd, J_1 = 17.8 Hz, J_2 = 8.6 Hz, 1H), 2.53-2.40 (m, 1H), 2.28-2.13 (m, 3H), 1.58-1.47 (m, 1H), 1.47-1.19 (m, 11H), 0.96-0.80 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 140.2, 107.0, 89.7, 41.0, 35.6, 34.8, 34.3, 31.5, 28.7, 27.8, 22.4, 20.4, 14.0, 13.9; IR (neat) ν = 2957, 2927, 2856, 1788, 1638, 1465, 1378, 1261, 1223, 1197, 1160, 985 cm^{-1}; MS (70 ev, EI) *m/z* (%) 364 (M^+, 29.05), 195 (100); HRMS Calcd for $C_{15}H_{25}IO_2$ (M^+): 364.0894, Found: 364.0891.

Procedure for the preparation of optically active 5-(1'-iodo-1'-alkenyl)-4,5-dihydro-2(3*H*)-furanones (*S*)-2a and (*S*)-2b

(1) Optically active 5-(1'-Iodo-1'-octenyl)-4,5-dihydro-2(3*H*)-furanone (mixture of (*S*)-*Z*-2a and (*R*)-*E*-2a). Typical Procedure.

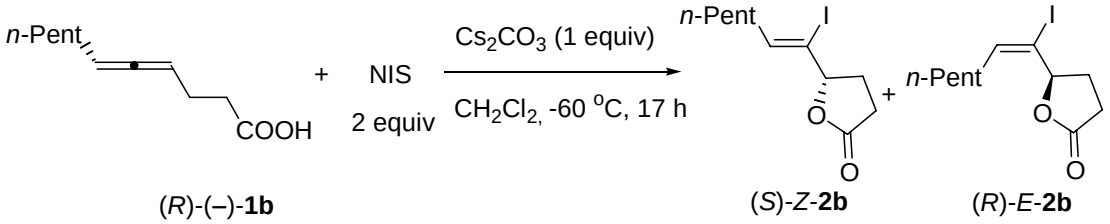


(*R*)-(–)-**1a** (*S*)-*Z*-**2a** (*R*)-*E*-**2a**

To a solution of (*R*)-(–)-**1a** (396.0 mg, 2 mmol) in CH_2Cl_2 (24 mL) was added Cs_2CO_3 (667.8 mg, 2 mmol) with stirring at rt. NIS (677.2 mg, 3 mmol) was then added to the mixture at –60 °C. After 10 h, another 0.5 equiv of NIS (0.2251 g, 1 mmol) was added at –60 °C. After the reaction was complete as monitored by TLC (eluent: petroleum ether/ethyl acetate = 5/1), the resulting mixture was warmed up to rt and quenched sequentially with H_2O (10 mL) and a sat. aqueous solution of

$Na_2S_2O_3$ (6 mL), extracted with ether (25 mL × 3), washed with brine, and dried over Na_2SO_4. After filtration, evaporation of the solvent, and chromatography on silica gel (petroleum ether/ethyl acetate/CH_2Cl_2 = 6/1/1) afforded **2a** (575.8 mg, 89%, (*S*)-*Z*-**2a** /(*R*)-*E*-**2a** = 85/15, (*S*)-*Z*-**2a** 99% ee, HPLC conditions: Chiralcel OJ-H column; rate, 0.5 mL/min; eluent, hexane/*i*-PrOH = 90/10; λ = 254 nm; t_R 14.8 (minor), 15.8 (major)): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ [6.44 (t, *J* = 7.6 Hz, 0.15H), 6.04 (td, J_1 = 7.0 Hz, J_2 = 0.9 Hz, 0.85H)], [4.89 (t, *J* = 7.0 Hz, 0.15H), 4.79 (t, *J* = 7.0 Hz, 0.85H)], 2.78-2.61 (m, 1H), 2.61-2.48 (m, 1H), 2.48-2.33 (m, 1H), 2.25-2.08 (m, 3H), 1.48-1.36 (m, 2H), 1.36-1.20 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H). This *Z*/*E* mixture was submitted to the kinetic resolution without further characterization.

(2) Optically active 5-(1'-Iodo-1'-heptenyl)-4,5-dihydro-2(3*H*)-furanone (mixture of (*S*)-*Z*-2b and (*R*)-*E*-2b)

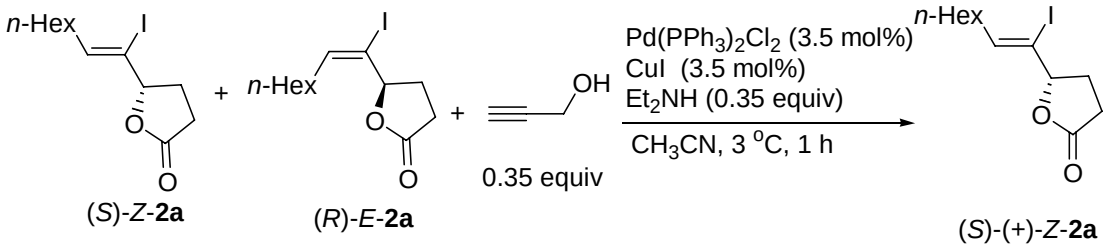


(*R*)-(–)-**1b** (*S*)-*Z*-**2b** (*R*)-*E*-**2b**

The reaction of (*R*)-(–)-**1b** (90.5 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) with Cs_2CO_3 (163.0 mg, 0.5 mmol) and NIS (in two portions: 167.9 mg + 56.3 mg, 1 mmol) afforded **2b** (138.9 mg, 91%, (*S*)-*Z*-**2b**/(*R*)-*E*-**2b** = 79/21, (*S*)-*Z*-**2b** > 98% ee, HPLC conditions: Chiralcel OJ-H column; rate, 0.5 mL/min; eluent, hexane/*i*-PrOH = 90/10; λ = 254 nm; t_R 18.7 (minor), 20.1 (major)): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ [6.44 (t, *J* = 7.8 Hz, 0.21H), 6.05 (t, *J* = 6.8 Hz, 0.79H)], [4.89 (t, *J* = 7.2 Hz, 0.21H), 4.79 (t, *J* = 7.0 Hz, 0.79H)], 2.76-2.60 (m, 1H), 2.60-2.48 (m, 1H), 2.48-2.31 (m, 1H), 2.26-2.07 (m, 3H), 1.50-1.38 (m, 2H), 1.38-1.20 (m, 4H), 0.89 (t, *J* = 6.6 Hz, 3H).

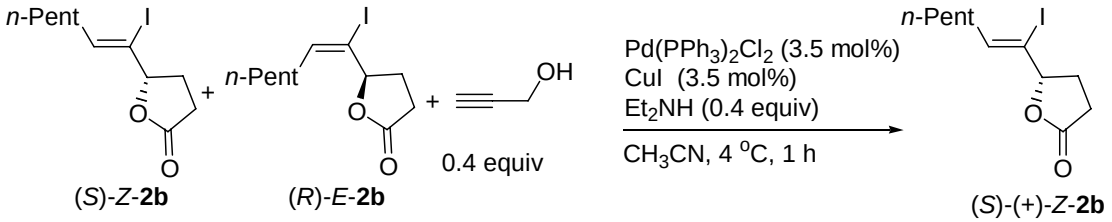
Procedure for the kinetic resolution of (*S*)-*Z*- and (*R*)-*E*-isomers of optically active products 2a and 2b

(1) (*S*)-(+)-5-(1'-Iodo-1'(*Z*)-octenyl)-4,5-dihydro-2(3*H*)-furanone ((*S*)-(+)-*Z*-2a). Typical Procedure.



To a mixture of CuI (2.1 mg, 3.5 mol%, 0.011 mmol) and $PdCl_2(PPh_3)_2$ (7.4 mg, 3.5 mol%, 0.011 mmol) was added a solution of Et_2NH (8.3 mg, 0.11 mmol), prop-2-yn-1-ol (5.4 mg, 0.096 mmol), and mixture of (*S*)-*Z*-**2a** and (*R*)-*E*-**2a** (95.8 mg, 0.3 mmol) in CH_3CN (1 mL). The mixture was stirred at 3 °C with an ice-water bath for 1 h under nitrogen. After the reaction was complete as monitored by GC, the resulting mixture was quenched with 10 mL of H_2O, diluted with 10 mL of ether, separated, extracted with ether (3 x 30 mL), washed with brine, and dried over Na_2SO_4. Filtration, evaporation, and purification by chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) afforded (*S*)-(+)-*Z*-**2a** (70.9 mg, 74%, *Z*/*E* = 98/2, 99% ee, HPLC conditions: Chiralcel OJ-H column; rate, 0.5 mL/min; eluent, hexane/*i*-PrOH = 90/10; λ = 254 nm; t_R 17.2 (minor), 18.3 (major)), the ^{1}H NMR date are the same as those for racemic *Z*-**2a**. $[\alpha]^{25}_D$ = +16.4 (*c* = 0.95, $CHCl_3$).

(2) (*S*)-(+)-5-(1'-Iodo-1'(*Z*)-heptenyl)-4,5-dihydro-2(3*H*)-furanone ((*S*)-(+)-*Z*-2b)

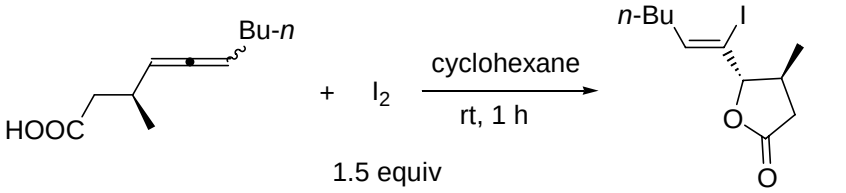


Following the procedure for the kinetic resolution of (*S*)-*Z*-**2a** and (*R*)-*E*-**2a,** the reaction of $PdCl_2(PPh_3)_2$ (7.4 mg, 3.5 mol%, 0.011 mmol), CuI (2.2 mg, 3.5 mol%, 0.011 mmol), Et_2NH (8.8 mg, 0.12 mmol), prop-2-yn-1-ol (7.3 mg, 0.13 mmol), and the mixture of (*S*)-*Z*-**2b** and (*R*)-*E*-**2b** (91.7 mg, 0.3 mmol) in CH_3CN (1 mL) at 4 °C for 1 h under nitrogen afforded (*S*)-(+)-*Z*-**2b** (58.2 mg, 63%, *Z*/*E* = 96/4, > 98% ee, HPLC conditions: Chiralcel OJ-H column; rate, 0.5 mL/min; eluent, hexane/*i*-PrOH = 90/10; λ = 254 nm; t_R 18.9 (minor), 20.4 (major)). The ^{1}H NMR date are the same as those for racemic *Z*-**2b**. $[\alpha]^{25}_D$ = +17.2 (*c* = 0.91, $CHCl_3$).

General procedure for the preparation of optically active

***trans*-4,5-dihydro-2(3*H*)-furanone (4*S*, 5*S*)-(+)-*Z*-2l, (4*S*, 5*S*)-(+)-*Z*-2m, (4*R*, 5*R*)-(–)-*Z*-2l**

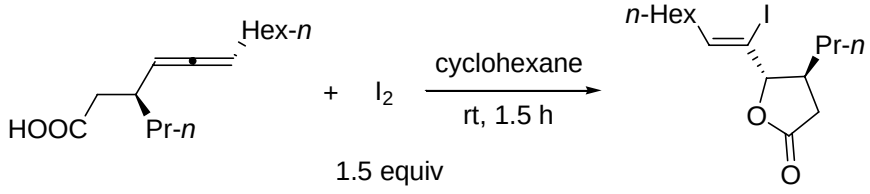
(1) (4*S*, 5*S*)-(+)-5-(1'-Iodo-1'(*Z*)-hexenyl)-4-methyl-4,5-dihydro-2(3*H*)-furanone ((4*S*, 5*S*)-(+)-*Z*-2l)



(*S*)-(+)-**1l** (4*S*, 5*S*)-(+)-*Z*-**2l**

To a solution of (*S*)-(+)-**1l** (53.6 mg, 0.3 mmol) in cyclohexane (4 mL) was added I_2 (114.3 mg, 0.45 mmol) with stirring at room temperature. After the reaction was complete (1 hour) as monitored by TLC (eluent: petroleum ether/ethyl acetate = 5/1), it was quenched with H_2O (6 mL) and sat. aqueous $Na_2S_2O_3$ (4 mL). The mixture was extracted with ether (20 mL × 3), washed with brine, and dried over Na_2SO_4. After filtration, evaporation of the solvent, and chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded (4*S*, 5*S*)-(+)-*Z*-**2l** (78.3 mg, 86%, *Z*/*E* = 98/2, 99% ee), HPLC conditions: Chiralcel OJ-H column; rate, 0.5 mL/min; eluent, hexane/*i*-PrOH = 90/10; λ = 254 nm; t_R 14.2 (minor), 17.6 (major). The ^{1}H NMR date are the same as those for racemic *trans*-*Z*-**2l**. $[\alpha]^{20}_D$ = +39.1 (*c* = 0.96, $CHCl_3$).

(2) (4*S*, 5*S*)-(+)-5-(1'-Iodo-1'(*Z*)-octenyl)-4-propyl-4,5-dihydro-2(3*H*)-furanone ((4*S*, 5*S*)-(+)-*Z*-2m)

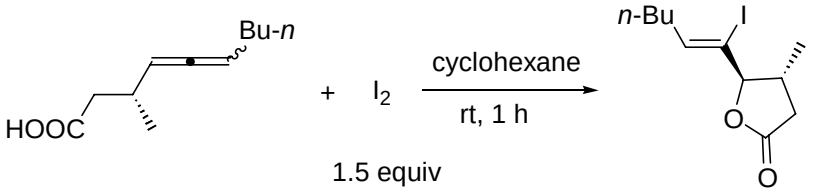


(*S*)-(+)-**1m** (4*S*, 5*S*)-(+)-*Z*-**2m**

The reaction of (*S*)-(+)-**1m** (34.9 mg, 0.15 mmol) in cyclohexane (2 mL) with I_2 (57.2 mg, 0.225 mmol) afforded (4*S*, 5*S*)-(+)-*Z*-**2m** (38.2 mg, 72%, *Z*/*E* = 96/4, 99% ee, HPLC conditions: Chiralcel OJ-H column; rate, 0.5 mL/min; eluent, hexane/*i*-PrOH = 95/5; λ = 254 nm, t_R 11.9 (minor), 12.9 (major)). The ^{1}H NMR date are the same as those for racemic *trans*-*Z*-**2m**. $[\alpha]^{20}_D$ = +40.0 (*c* = 1.2, $CHCl_3$).

(3) (4*R*, 5*R*)-(–)-5-(1'-Iodo-1'(*Z*)-hexenyl)-4-methyl-4,5-dihydro-2(3*H*)-furanone

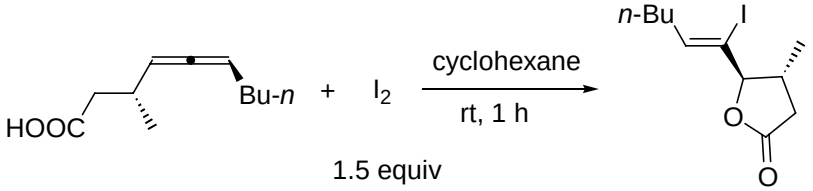
((4*R*, 5*R*)-(–)-*Z*-2l)



(*R*)-(–)-**1l** (4*R*, 5*R*)-(–)-*Z*-**2l**

The reaction of (*R*)-(–)-**1l** (36.5 mg, 0.2 mmol) in cyclohexane (2.7 mL) with I_2 (76.2 mg, 0.3 mmol) afforded (4*R*, 5*R*)-(–)-*Z*-**2l** (50.7 mg, 77%, *Z*/*E* = 97/3, 99% ee), HPLC conditions: Chiralcel OJ-H column (250 mm); rate, 0.5 mL/min; eluent, hexane/*i*-PrOH = 90/10; λ = 254 nm; t_R 14.3 (major), 18.0 (minor). The ^{1}H NMR date are the same as those for racemic *trans*-*Z*-**2l**. $[\alpha]^{20}_D$ = -38.5 (*c* = 1.76, $CHCl_3$).

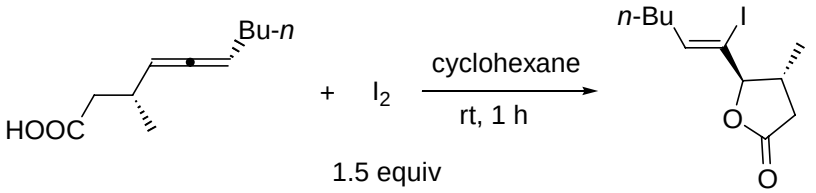
(4) (4*R*, 5*R*)-(–)-5-(1'-Iodo-1'(*Z*)-hexenyl)-4-methyl-4,5-dihydro-2(3*H*)-furanone ((4*R*, 5*R*)-(–)-*Z*-2l)



(R_a, *R*)-(–)-**1l** (4*R*, 5*R*)-(–)-*Z*-**2l**

To a solution of (R_a, *R*)-(–)-**1l** (19.2 mg, 0.1 mmol) in cyclohexane (1.3 mL) was added I_2 (38.4 mg, 0.15 mmol) with stirring at room temperature. After the reaction was complete (1 hour) as monitored by TLC (eluent: petroleum ether/ethyl acetate = 5/1), it was quenched with H_2O (2 mL) and sat. aqueous $Na_2S_2O_3$ (2 mL). The mixture was extracted with ether (20 mL × 3), washed with brine, and dried over Na_2SO_4. After filtration, evaporation of the solvent, and chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded (4*R*, 5*R*)-(–)-*Z*-**2l** (26.1 mg, 80%, *Z*/*E* = 97/3, 99% ee), HPLC conditions: Chiralcel OJ-H column(250 mm); rate, 0.5 mL/min; eluent, hexane/*i*-PrOH = 90/10; λ = 254 nm; t_R 13.7 (major), 17.1 (minor). The ^{1}H NMR date are the same as those for racemic *trans*-*Z*-**2l**. $[\alpha]^{20}_D$ = -34.4 (*c* = 0.74, $CHCl_3$).

(5) (4*R*, 5*R*)-(–)-5-(1'-Iodo-1'(*Z*)-hexenyl)-4-methyl-4,5-dihydro-2(3*H*)-furanone ((4*R*, 5*R*)-(–)-*Z*-2l)



(S_a, *R*)-(+)-**1l** (4*R*, 5*R*)-(–)-*Z*-**2l**

The reaction of (S_a, *R*)-(+)-**1l** (10 mg, 0.055 mmol) in cyclohexane (0.7 mL) with I_2 (21 mg, 0.082 mmol) afforded (4*R*, 5*R*)-(–)-*Z*-**2l** (13 mg, 77%, *Z*/*E* = 97/3, 99% ee), HPLC conditions: Chiralcel OJ-H column(150 mm); rate, 0.5 mL/min; eluent, hexane/*i*-PrOH = 90/10; λ = 254 nm; t_R 8.5 (major), 10.5 (minor). The ^{1}H NMR date are the same as those for racemic *trans*-*Z*-**2l**. $[\alpha]^{20}_D$ = -38 (*c* = 0.5, $CHCl_3$).

References:

[1] C. Jonasson, A. Horváth, J.-E. Bäckvall, *J. Am. Chem. Soc*. **2000**, *122*, 9600.

[2] S. Arseniyadis, J. Gore, M. L. Roumestant, *Tetrahedron* **1979**, *35*, 353.

[3] J. N. Shooiery, *Prog. NMR Spectrosc.* **1977**, *11*, 79.

[4] K. Mori, T. Nukada, T. Ebata, *Tetrahedron* **1981**, *37*, 1343.

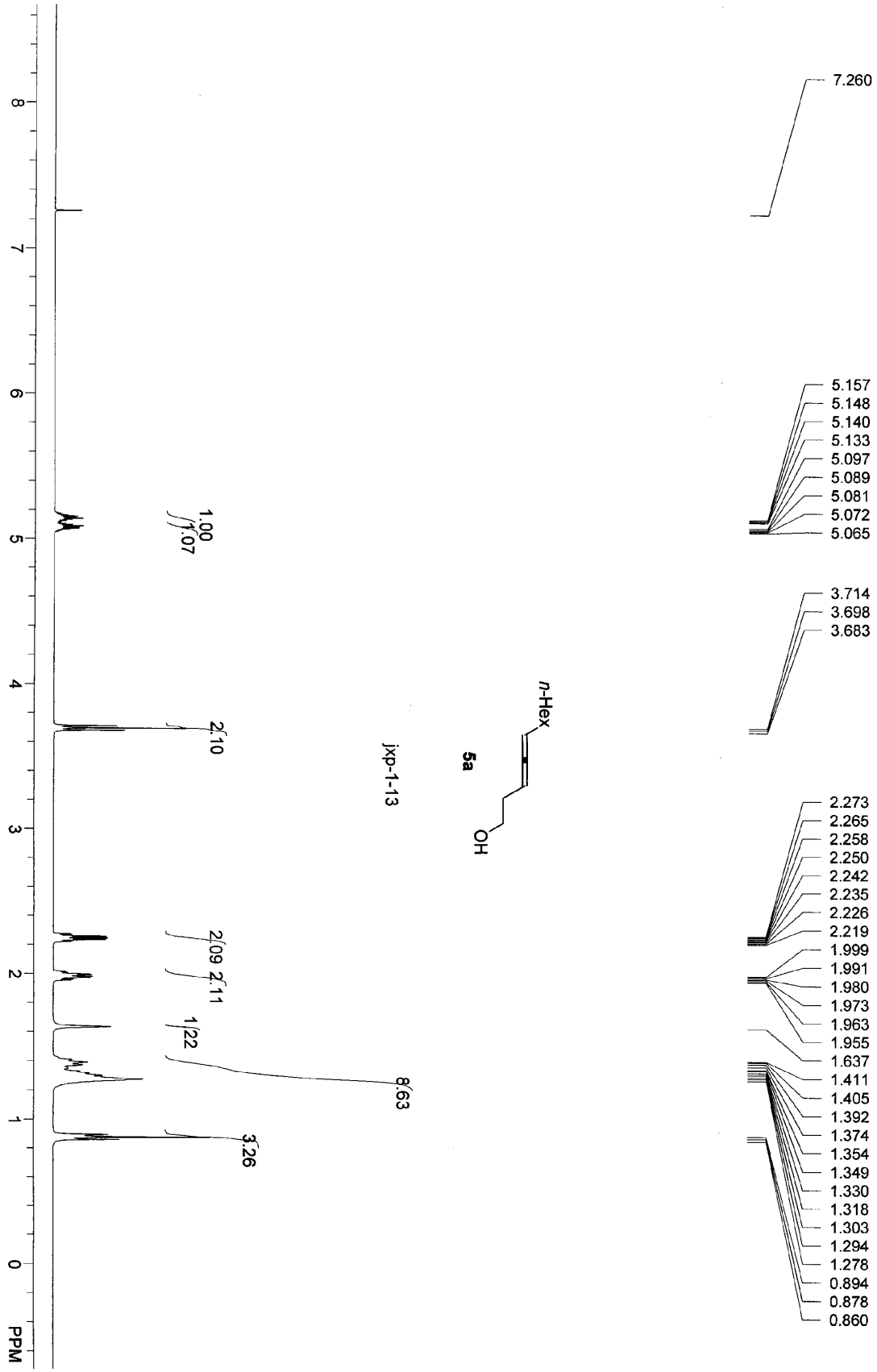
[5] C. Zhu, X. Shen, S. G. Nelson, *J. Am. Chem. Soc*. **2004**, *126*, 5352.

[6] N. J. Harris, J. J. Gajewski, *J. Am. Chem. Soc*. **1994**, *116*, 6121.

[7] When the TMS group was removed by its treatment with TBAF in THF, this desilylation led to serious epimerization of the axial chirality, thus, a pair of diastereoisomers was formed, see: C. Rameshkumar, R. P. Hsung, *Angew. Chem. Int. Ed.* **2004**, *43*, 615.

[8] Z. Wan, S. G. Nelson, *J. Am. Chem. Soc*. **2000**, *126*, 10470.

^{1}H NMR, ^{13}C NMR, and HPLC Spectra of all the compounds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2.242
2.235
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2.219
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1.980
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1.318
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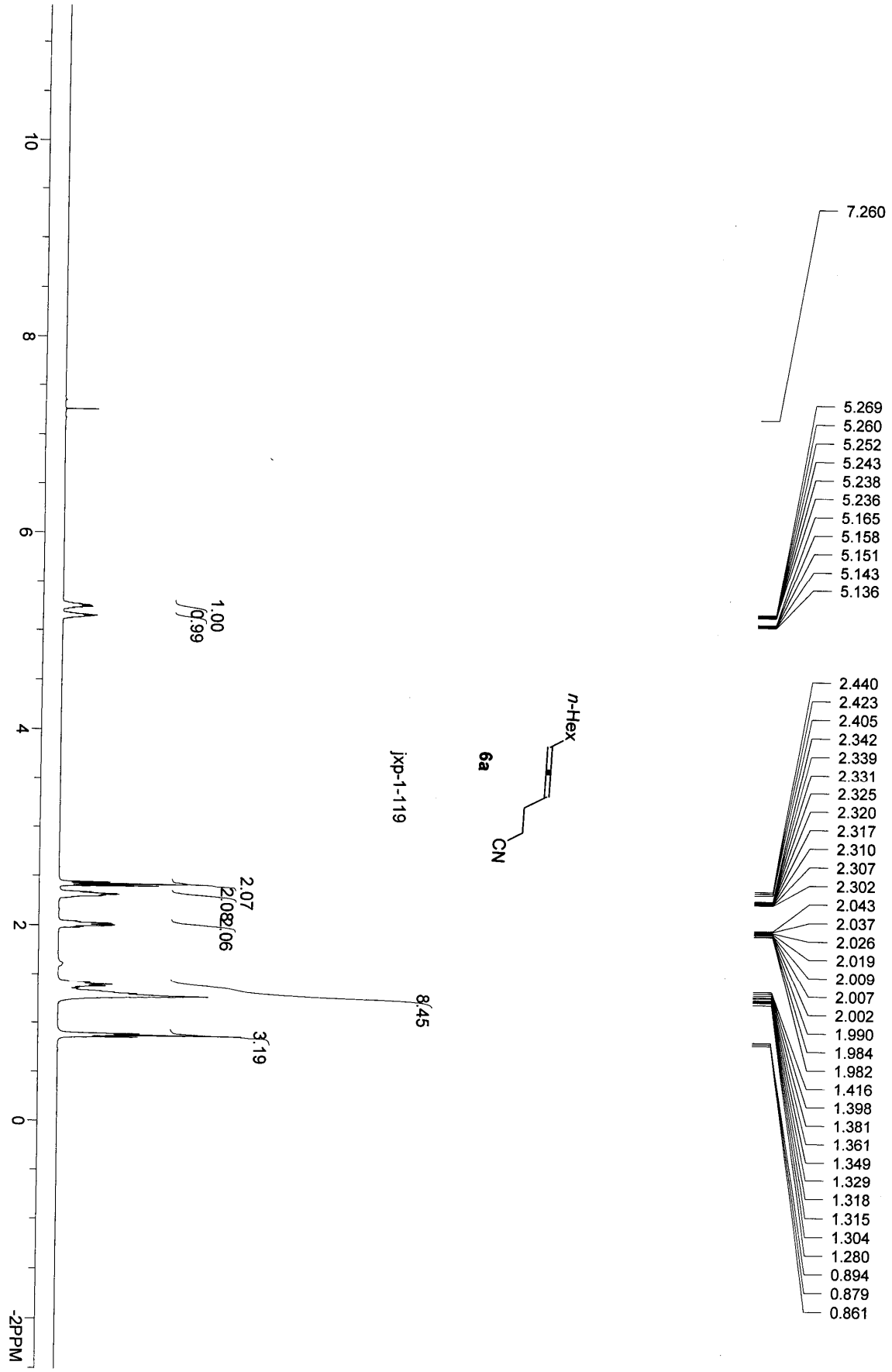
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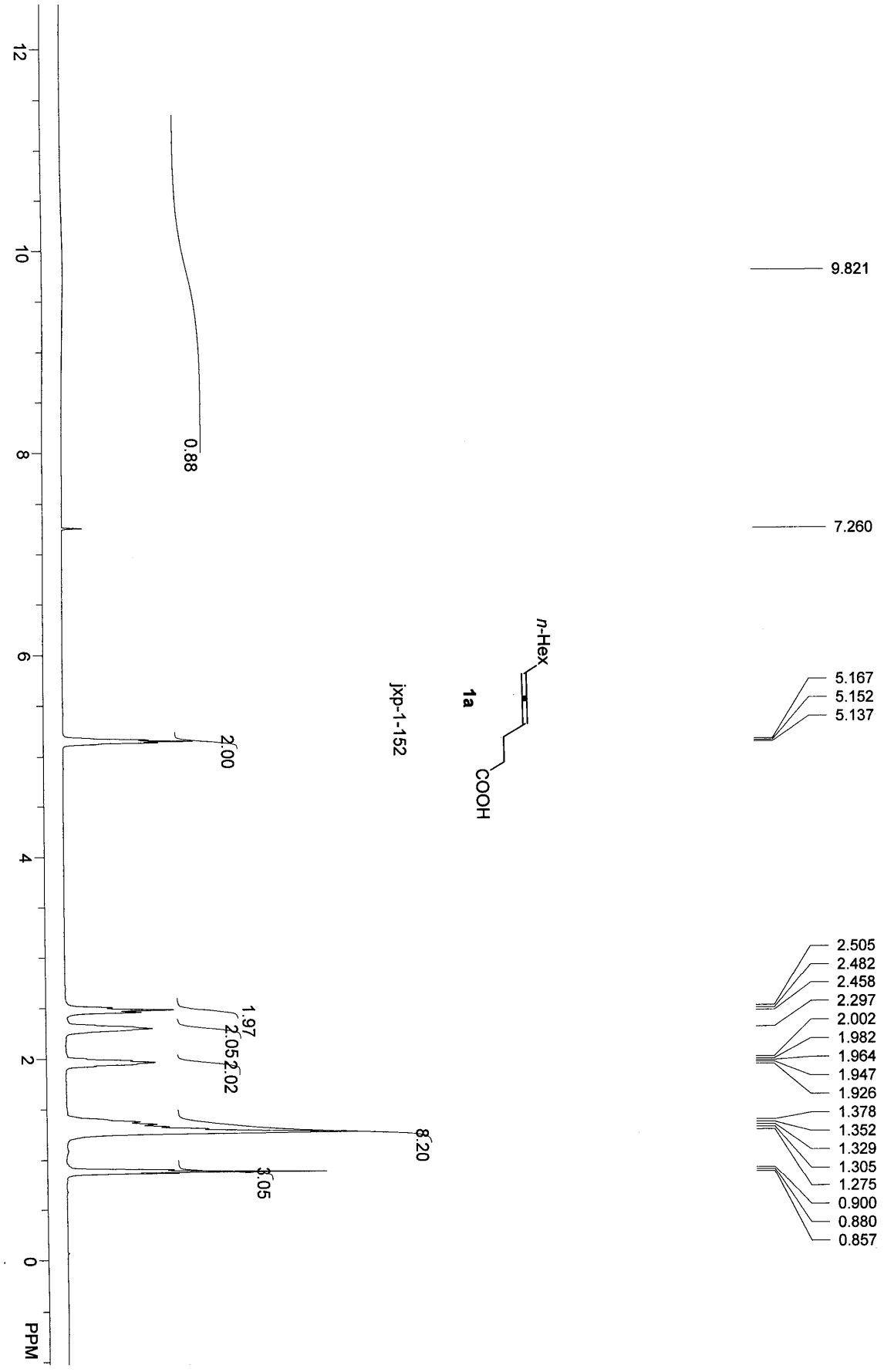
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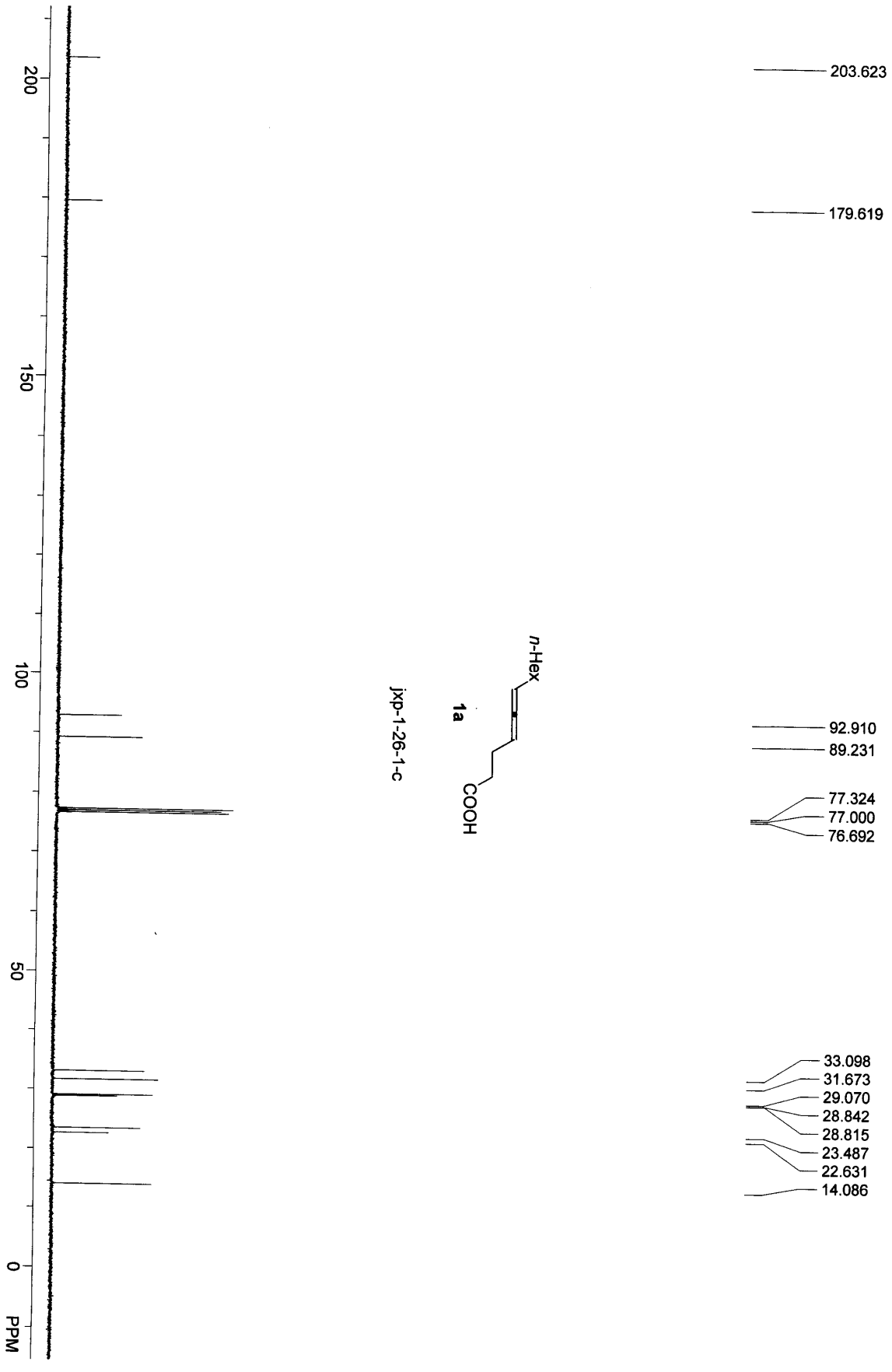
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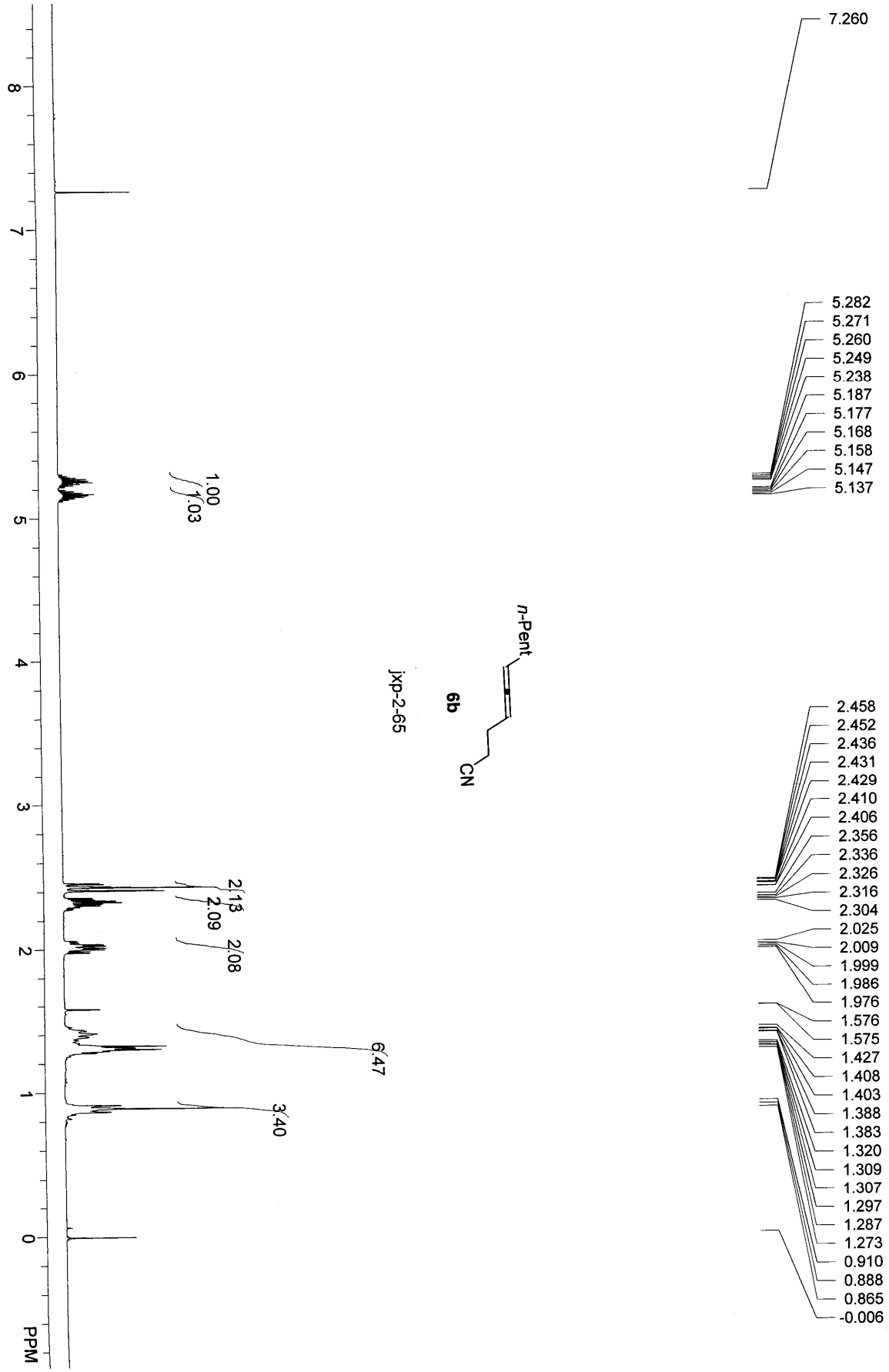
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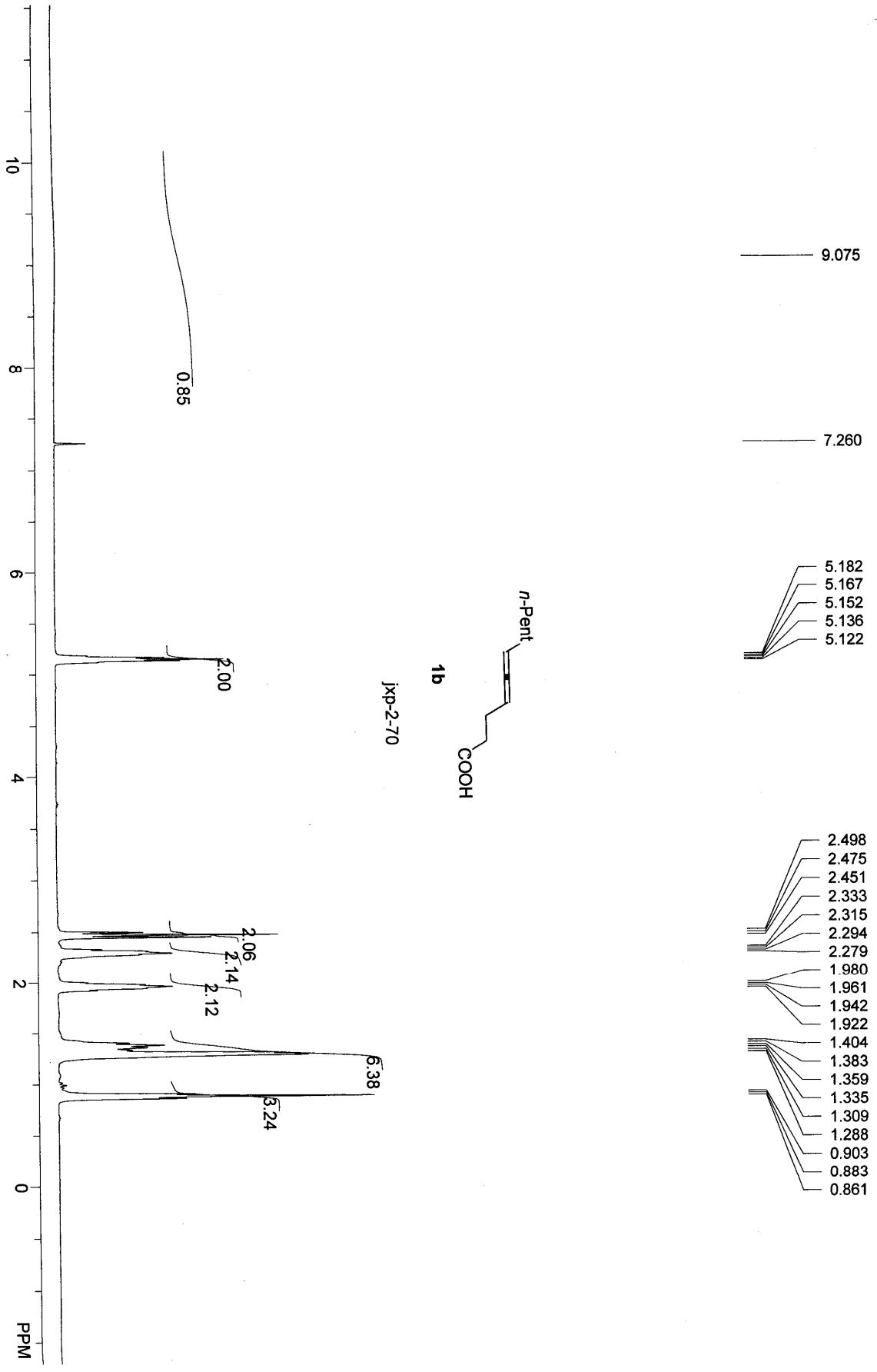
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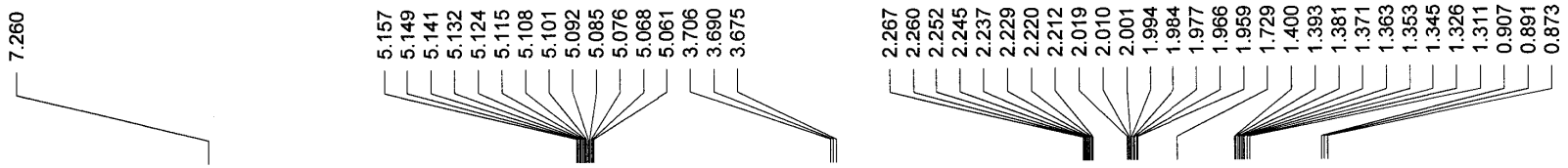
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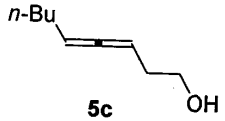
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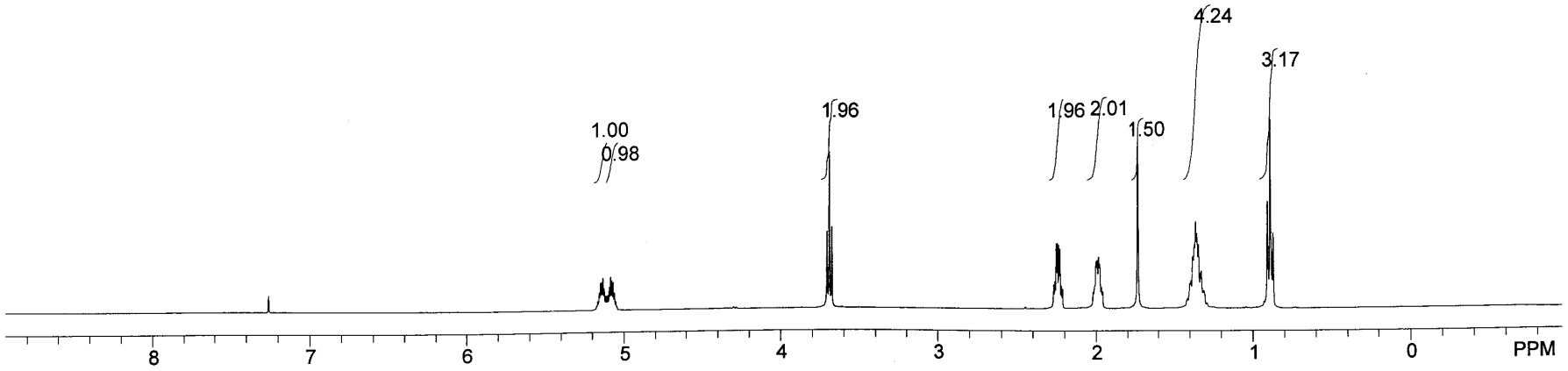
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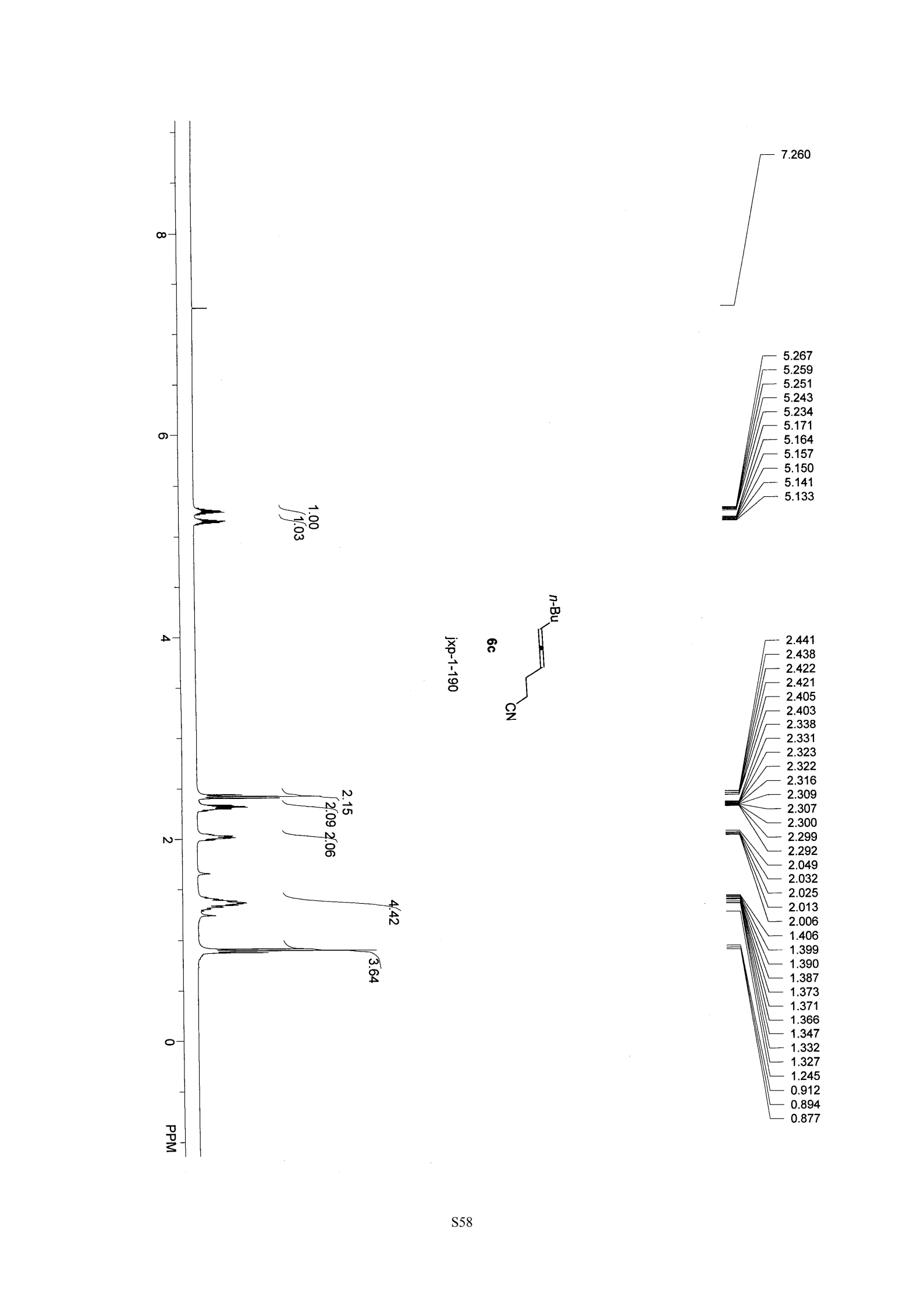
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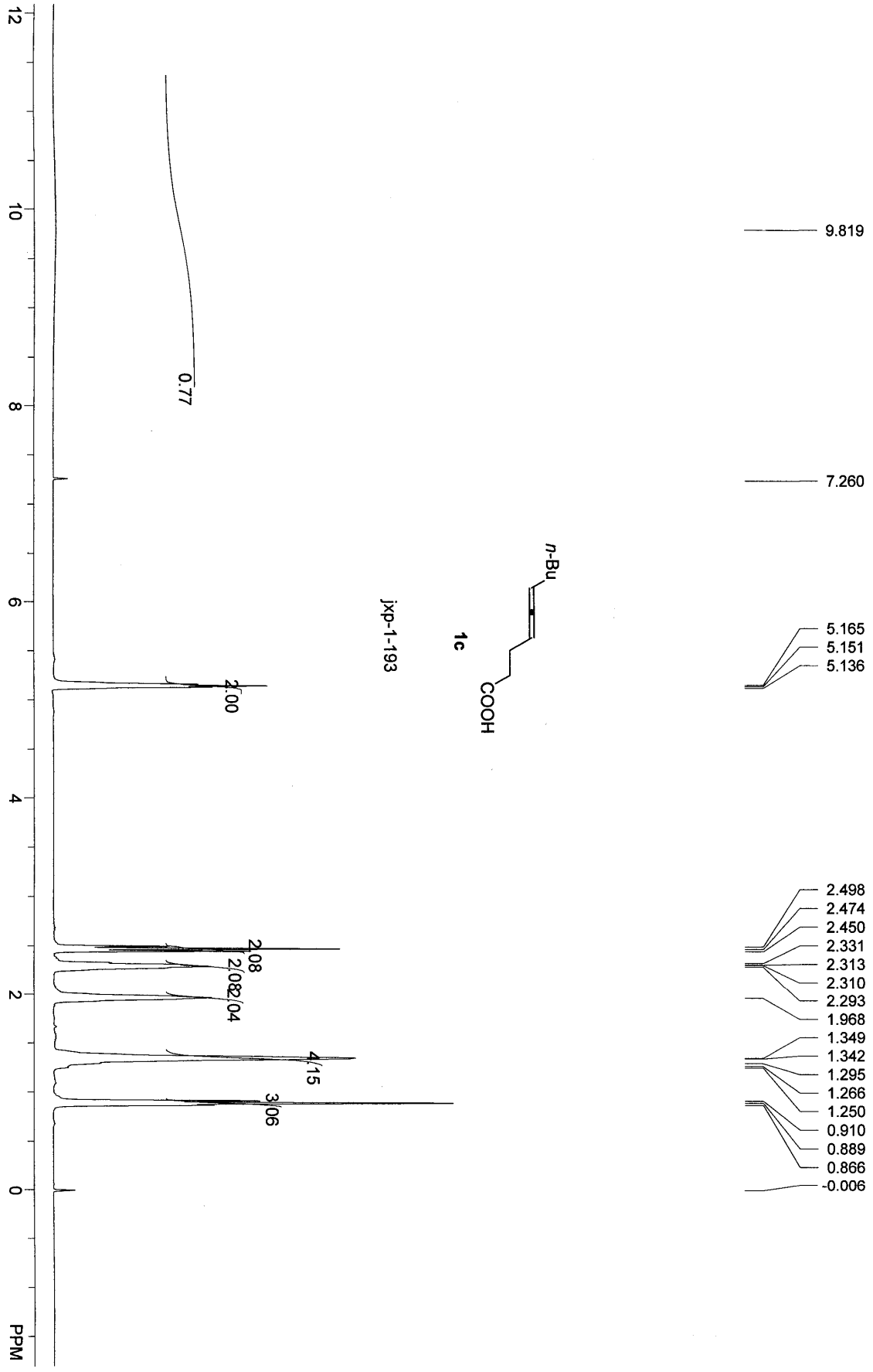
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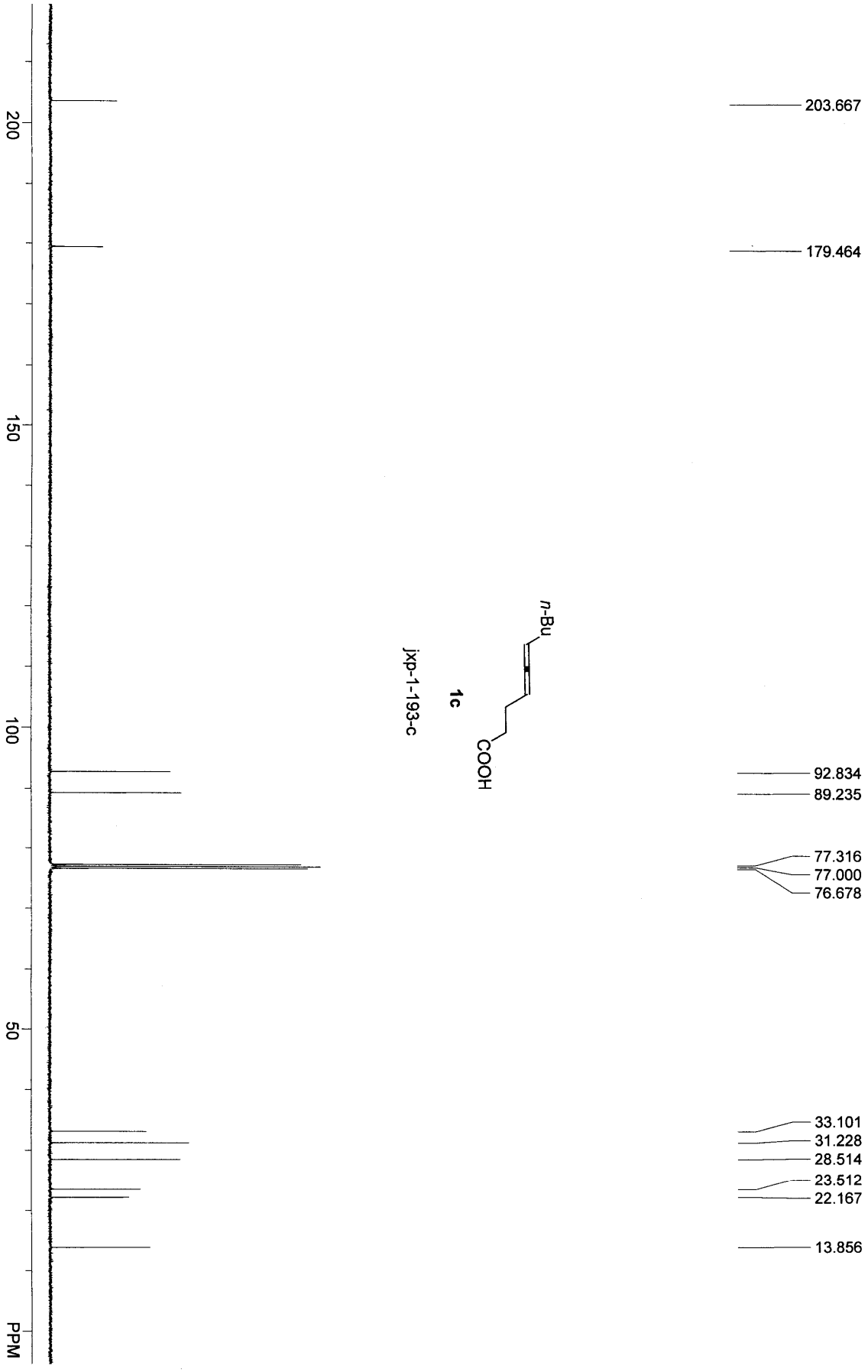
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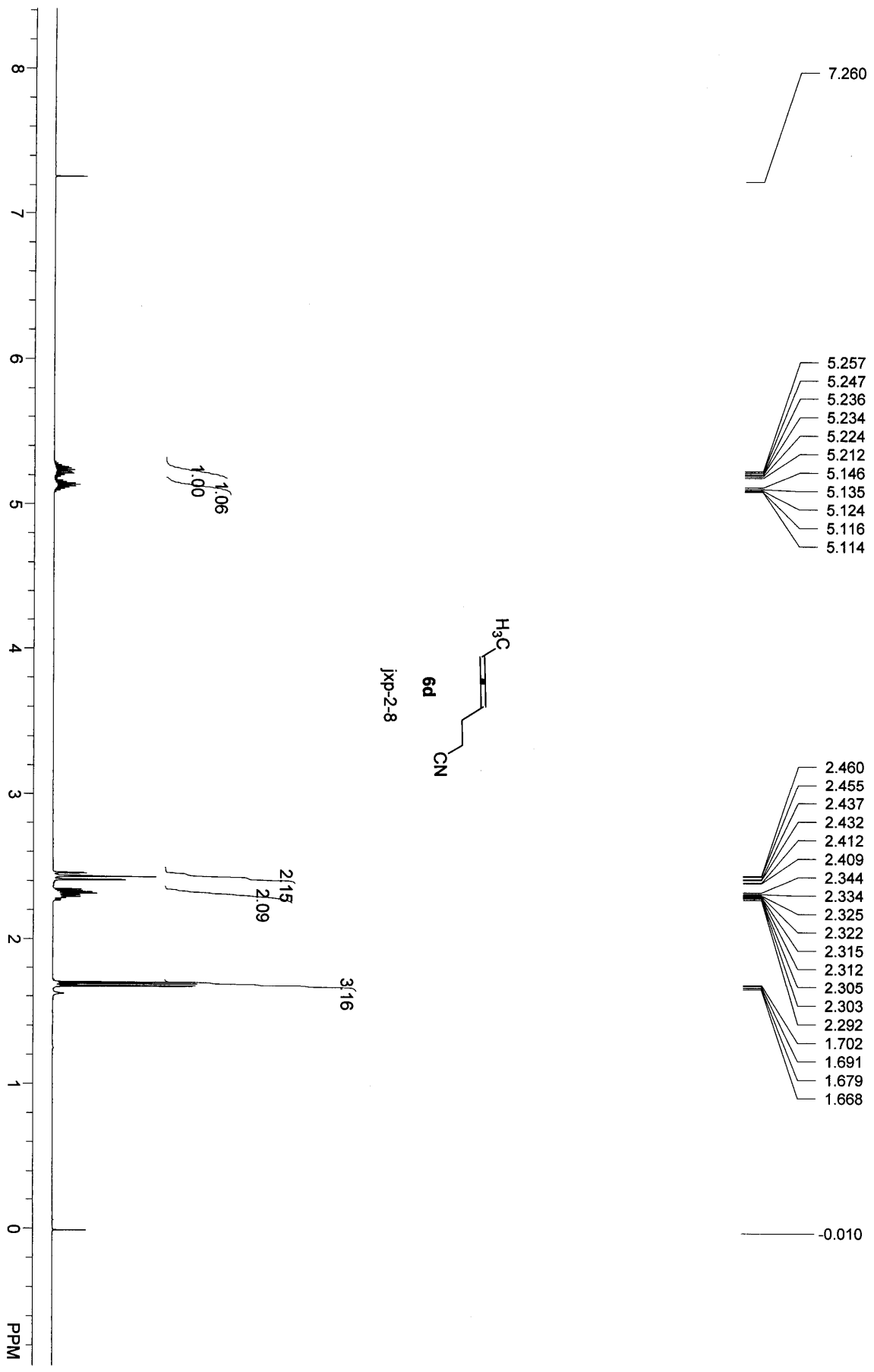
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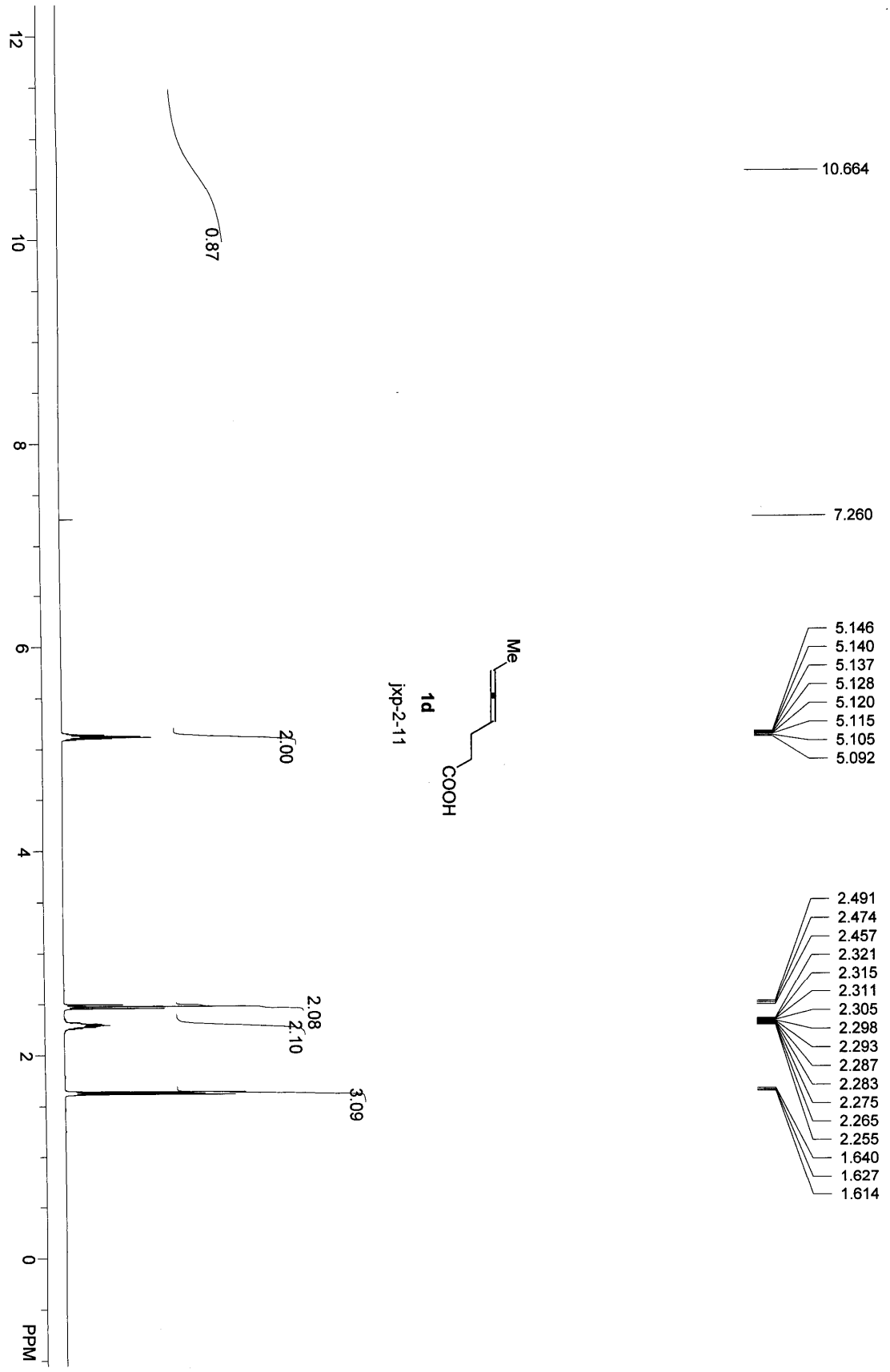
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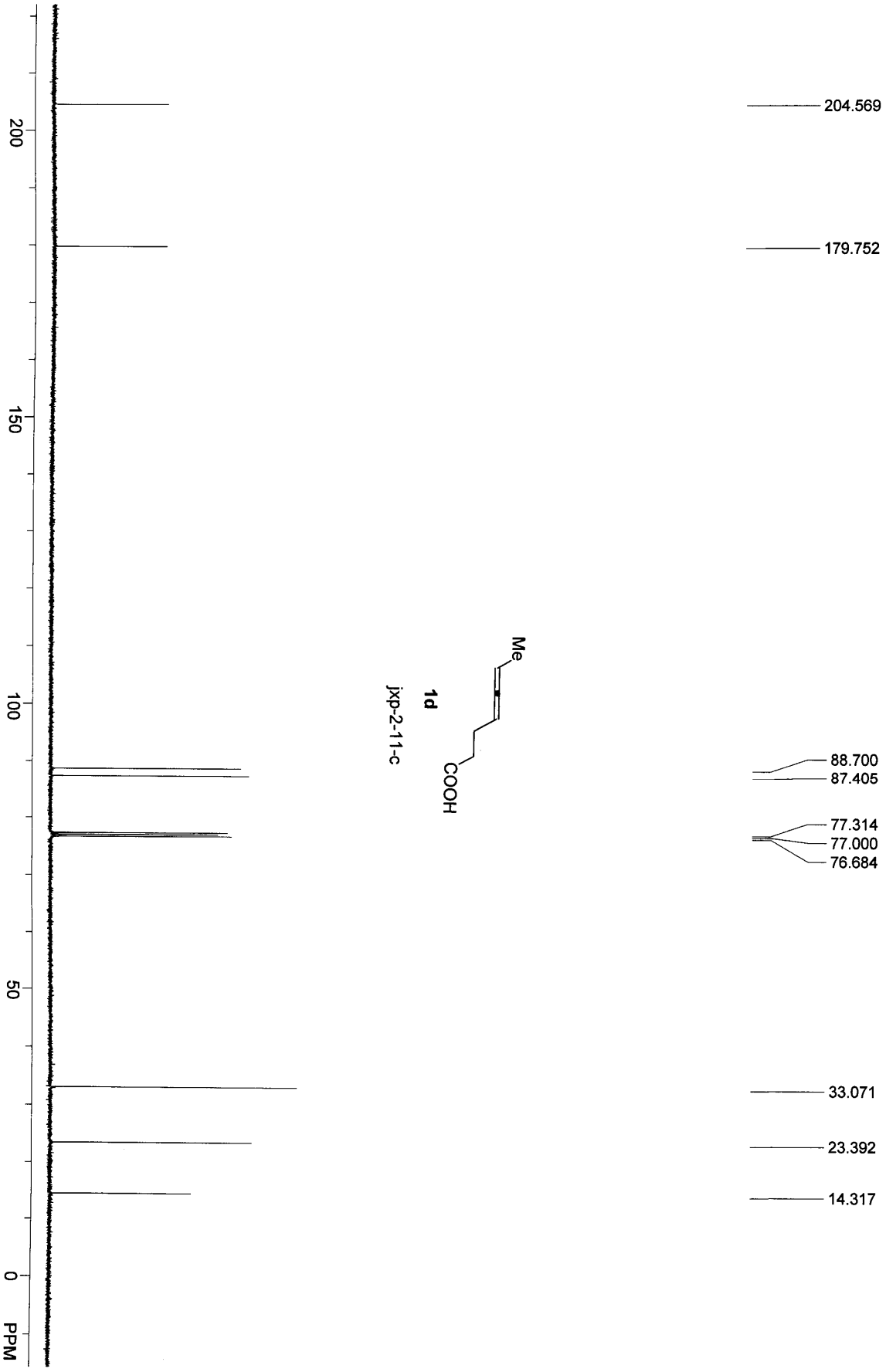
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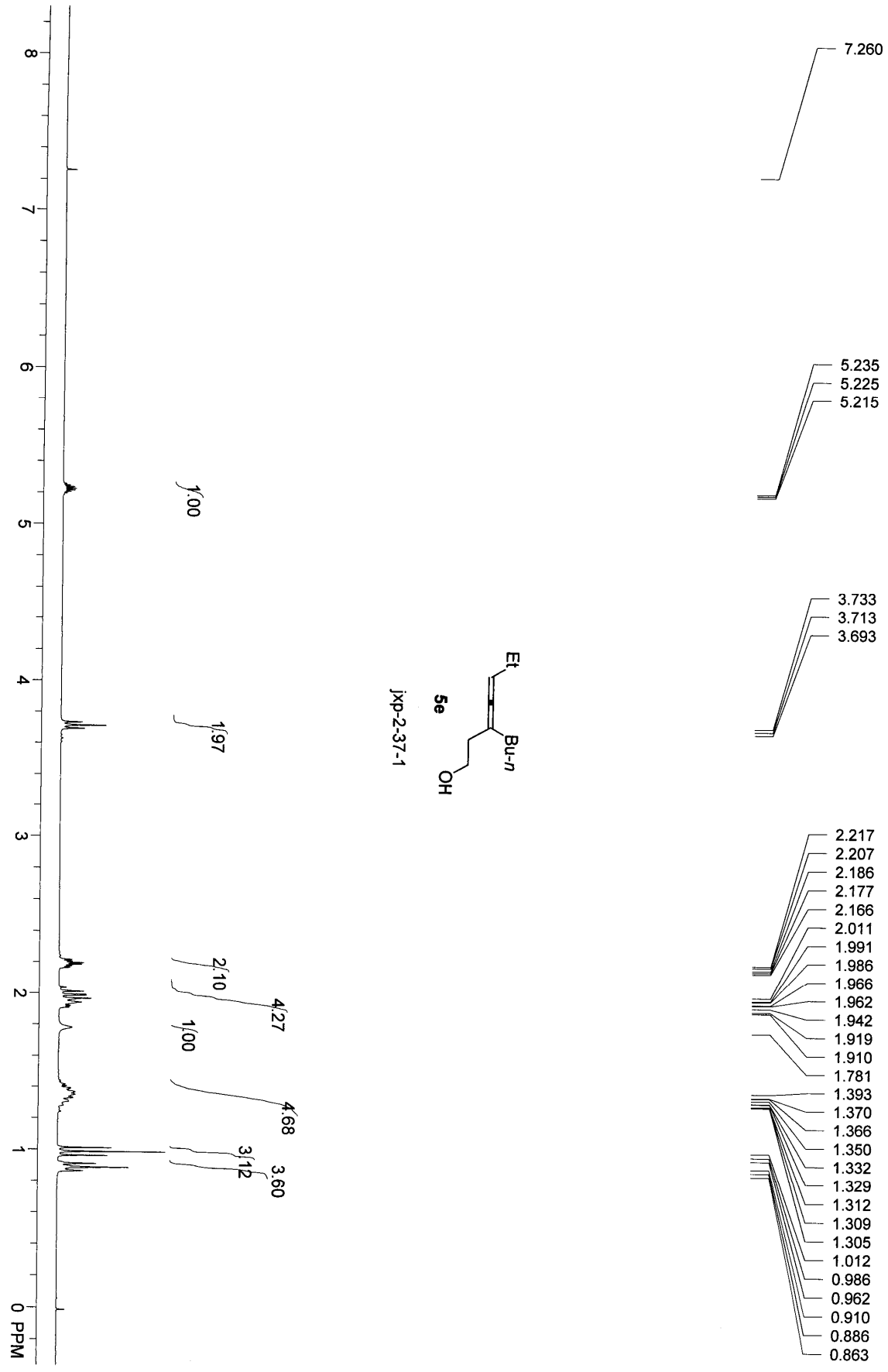
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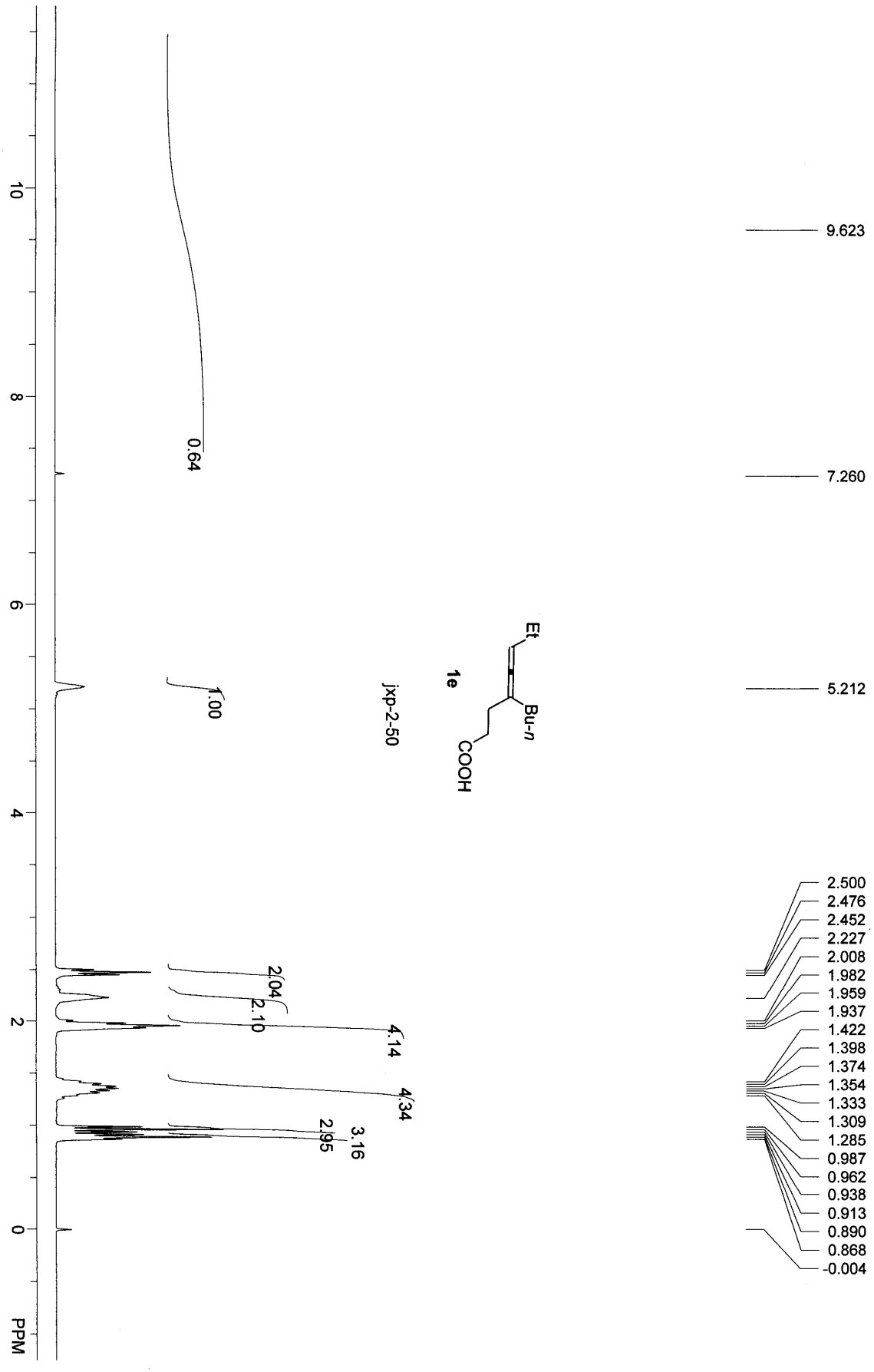
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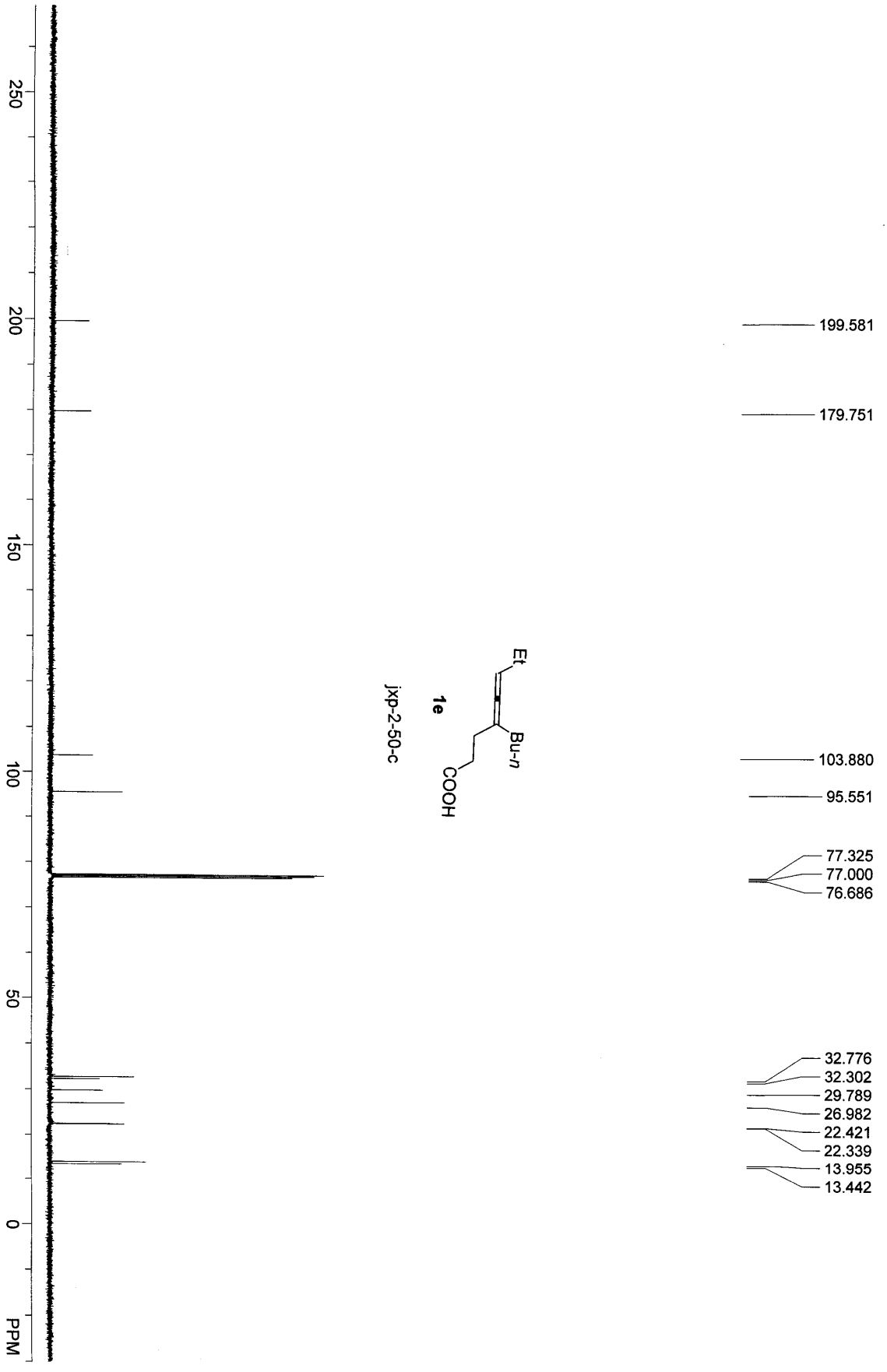
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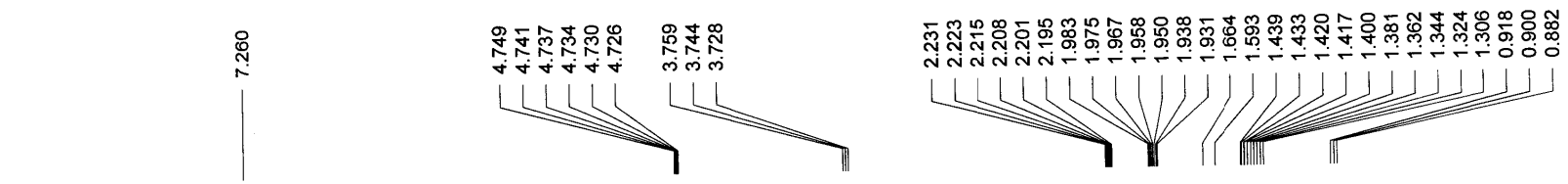
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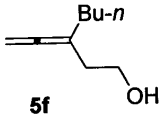
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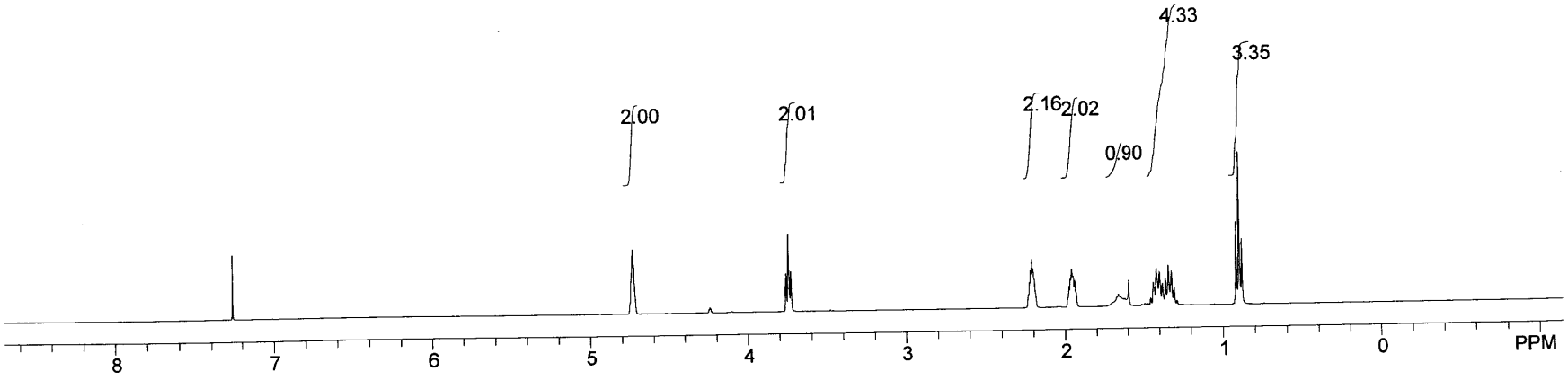
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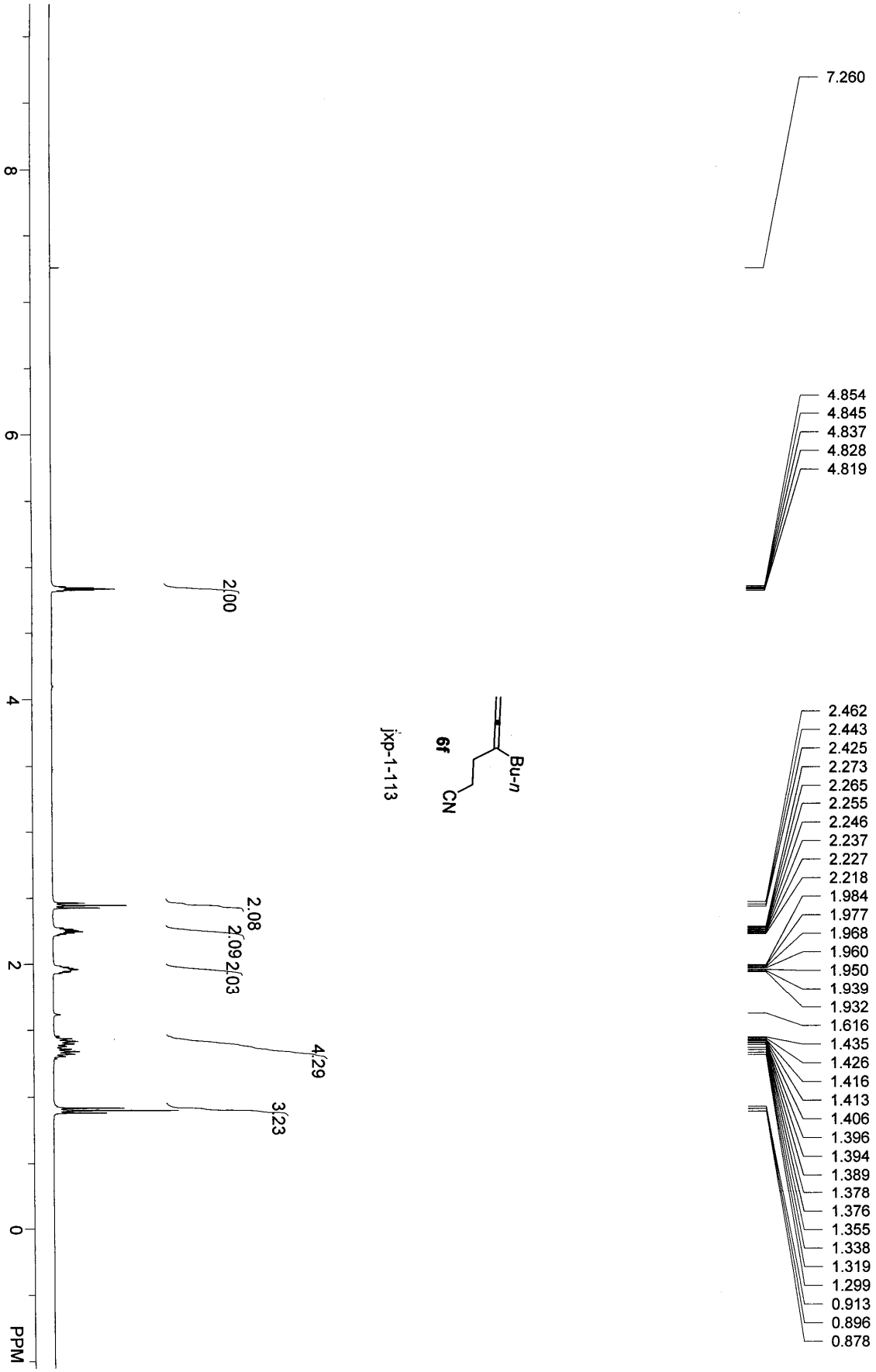
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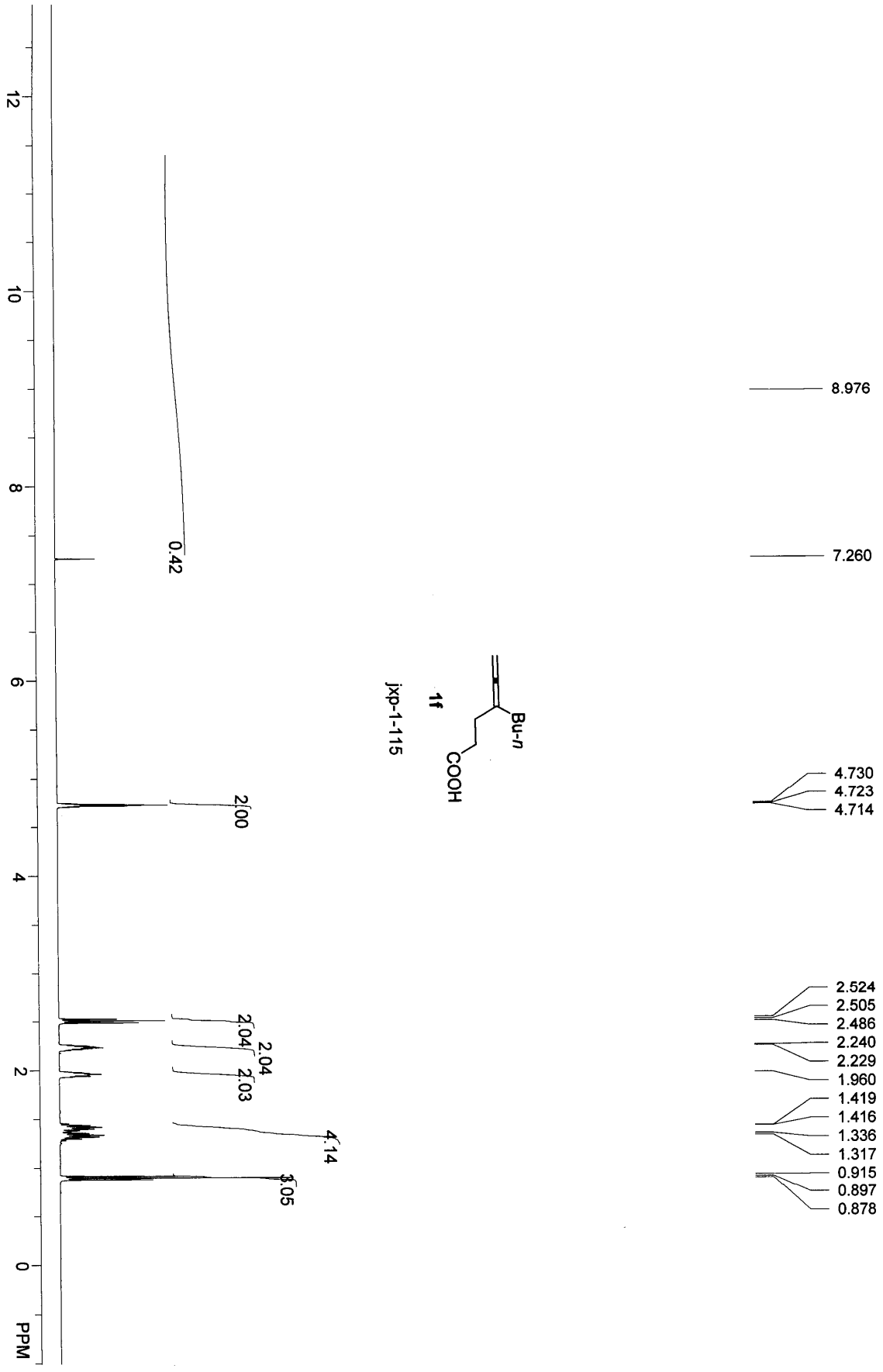
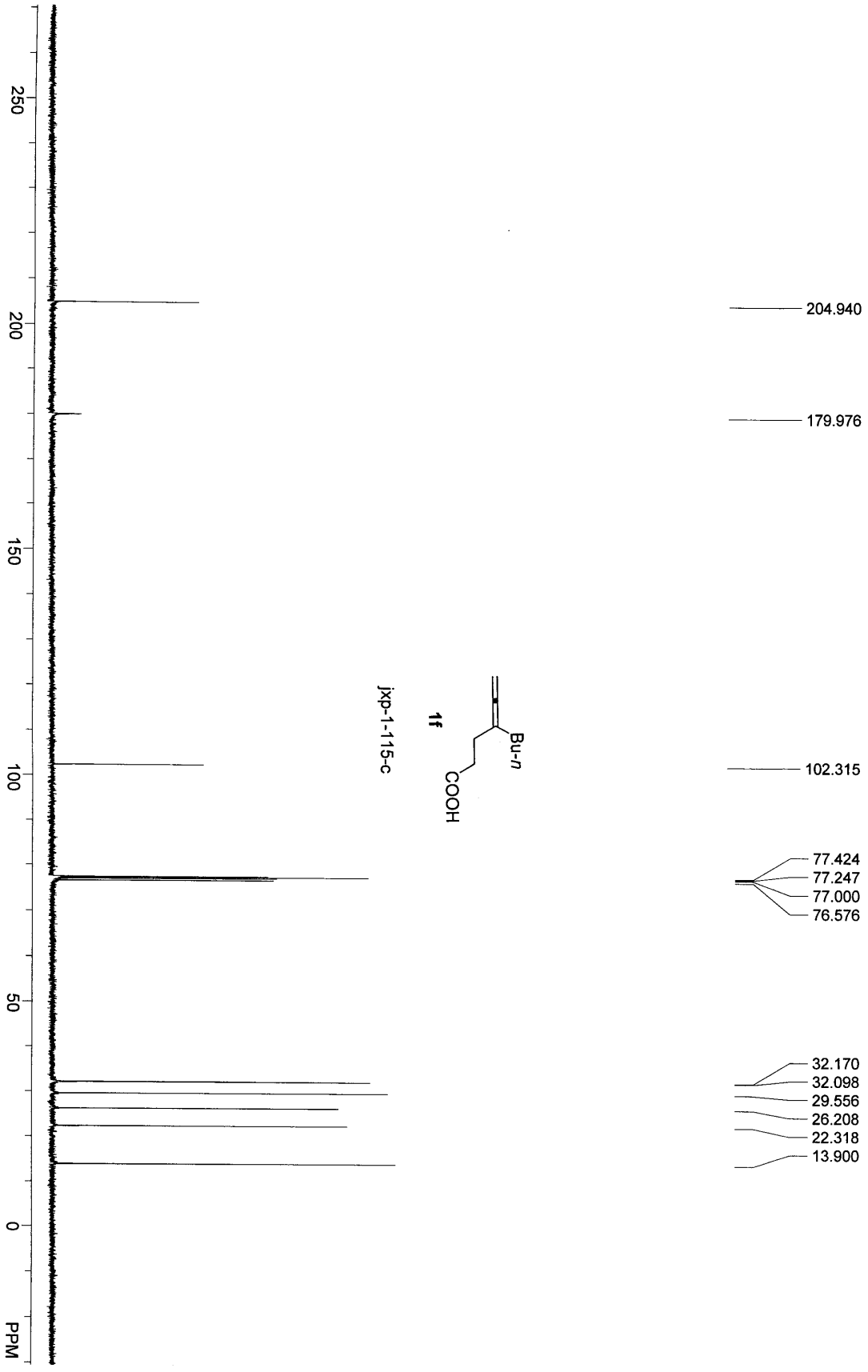
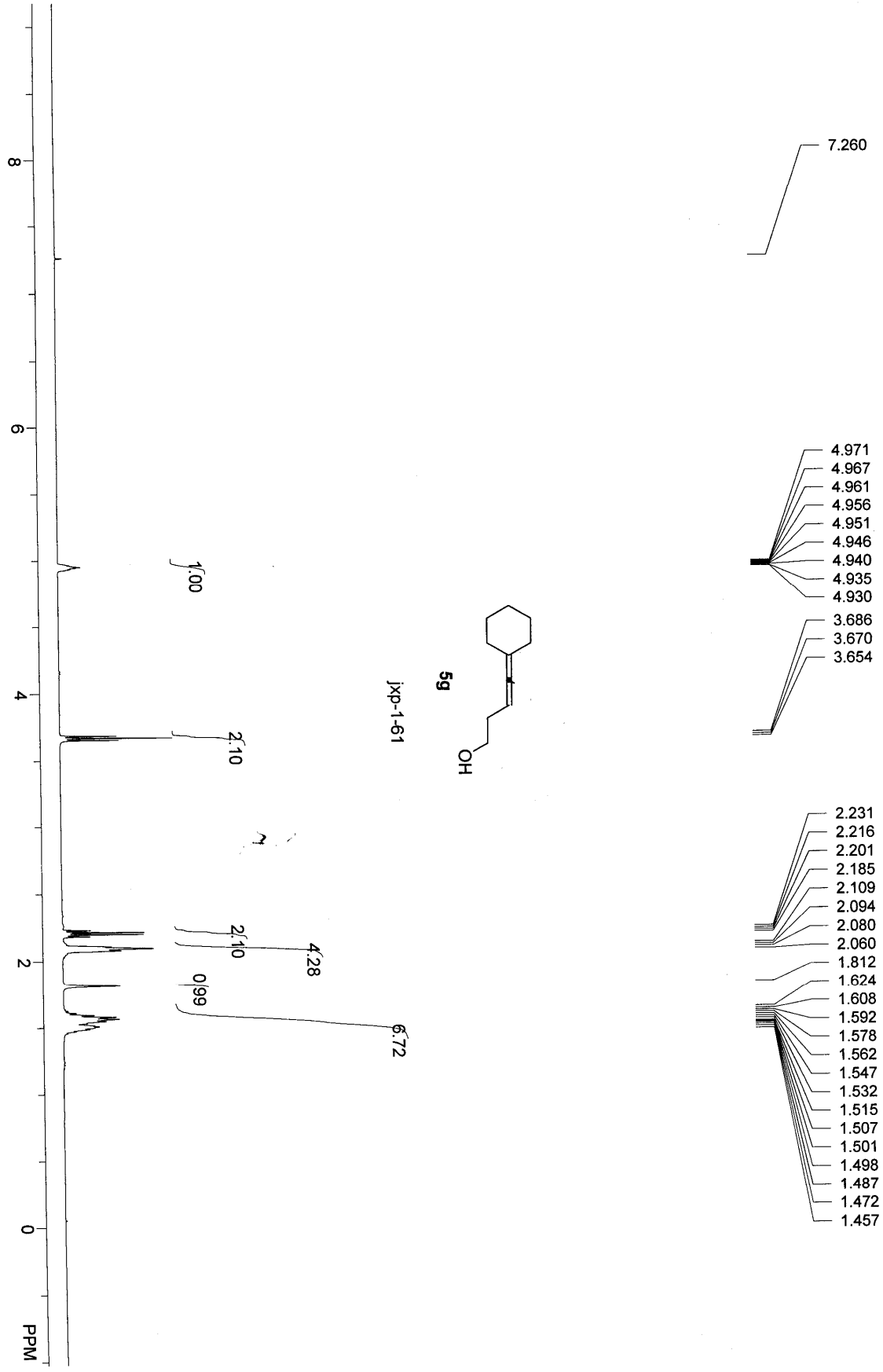
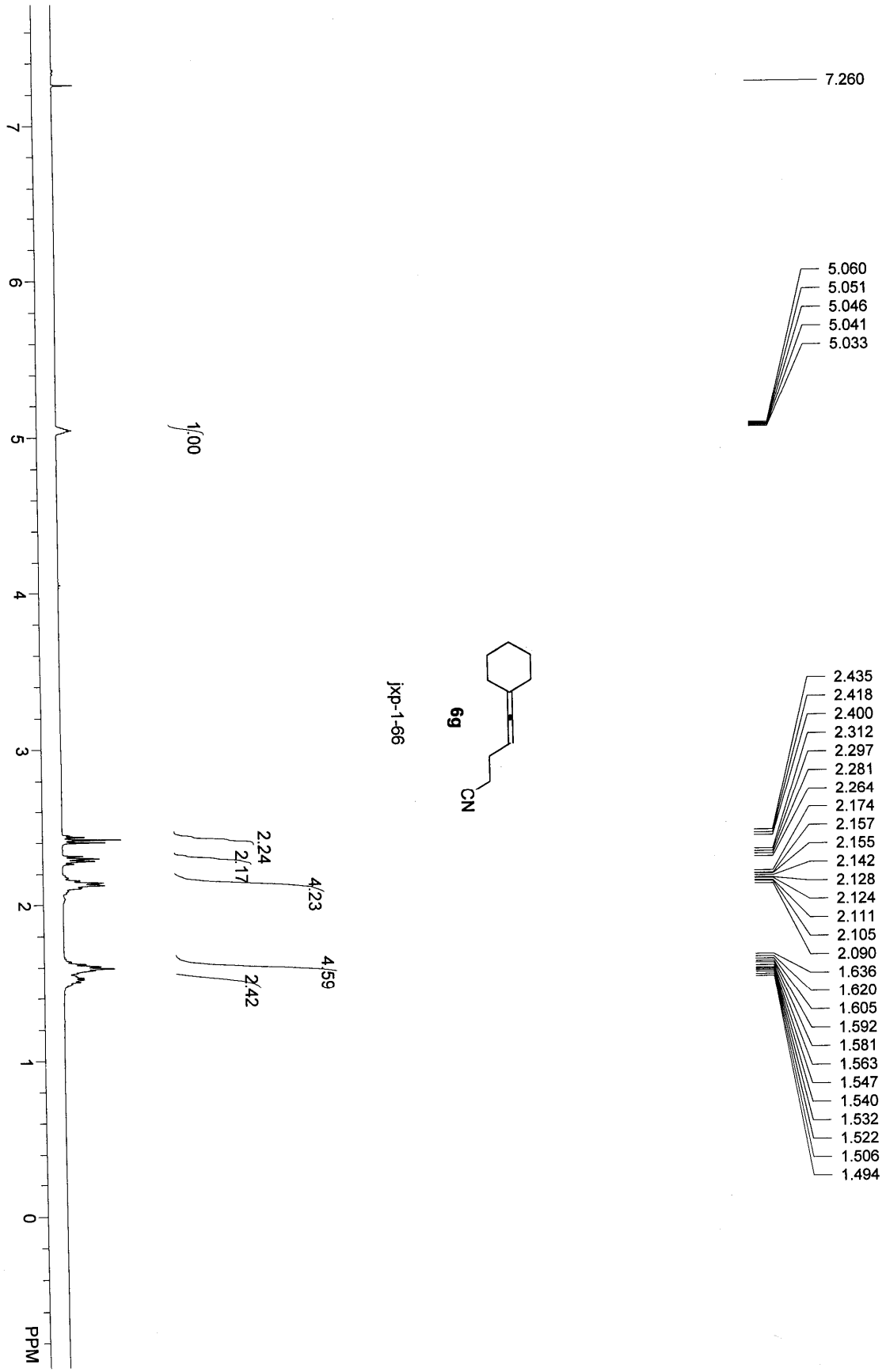
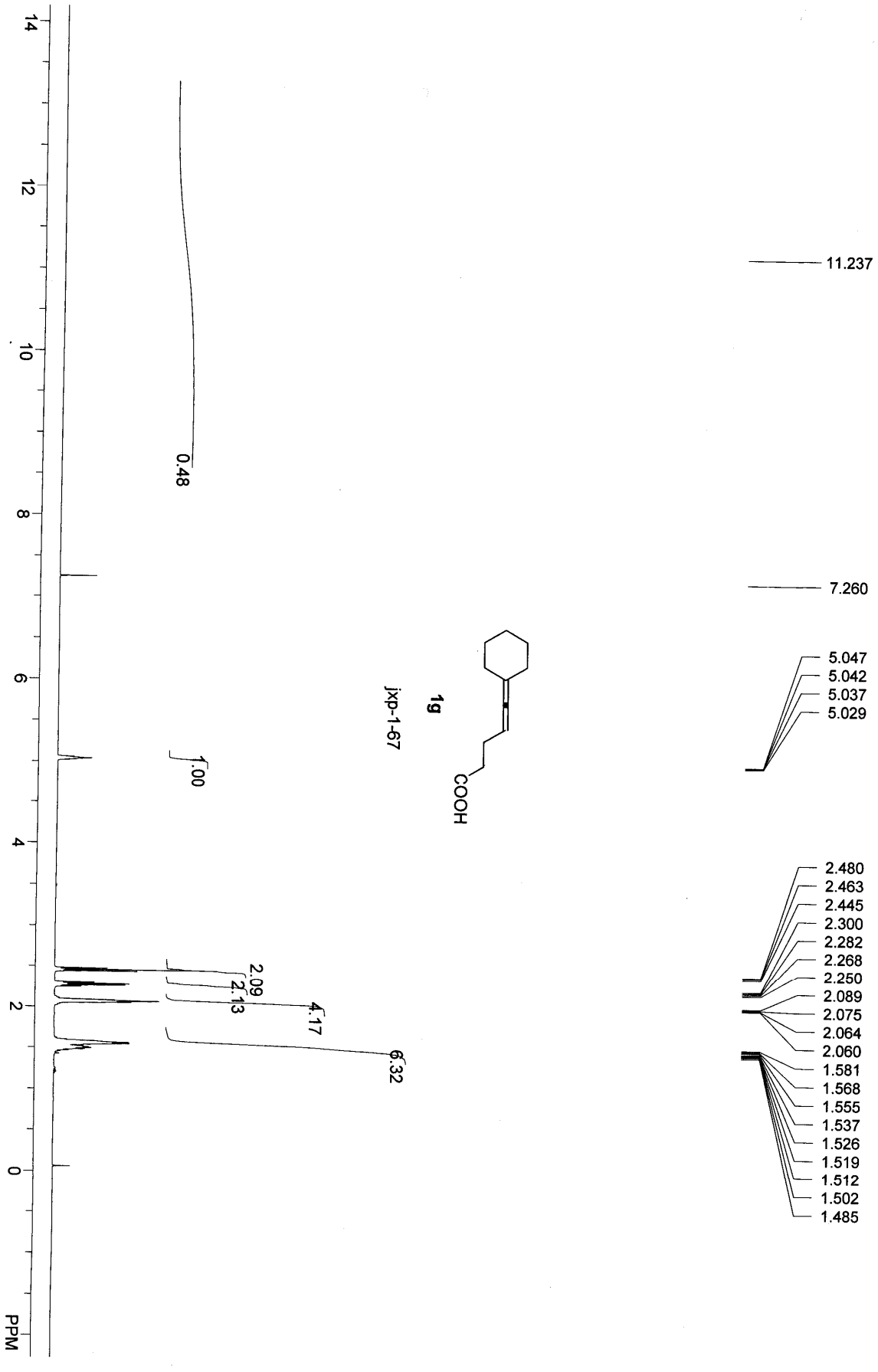
1.319
1.299
0.913
0.896
0.878
2.00
2.08
2.09
2.03
4.29
3.23
8
6
4
2
0
PPM
jxp-1-113
6f
Bu-n
CN

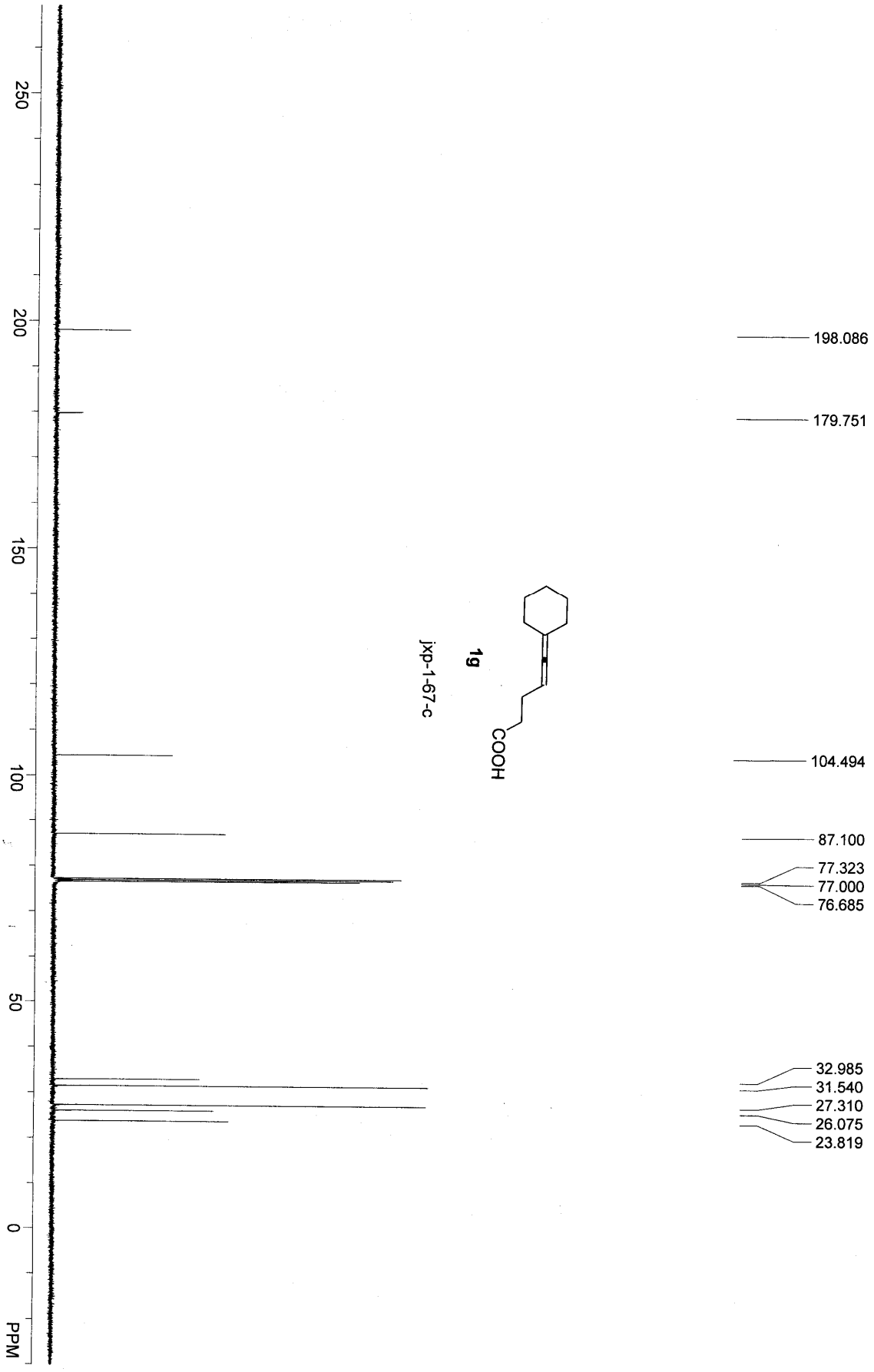

12
10
8
6
4
2
0
PPM
0.42
2.00
2.04
2.04
2.03
4.14
3.05
jxp-1-115
1f
COOH
Bu-n
8.976
7.260
4.730
4.723
4.714
2.524
2.505
2.486
2.240
2.229
1.960
1.419
1.416
1.336
1.317
0.915
0.897
0.878

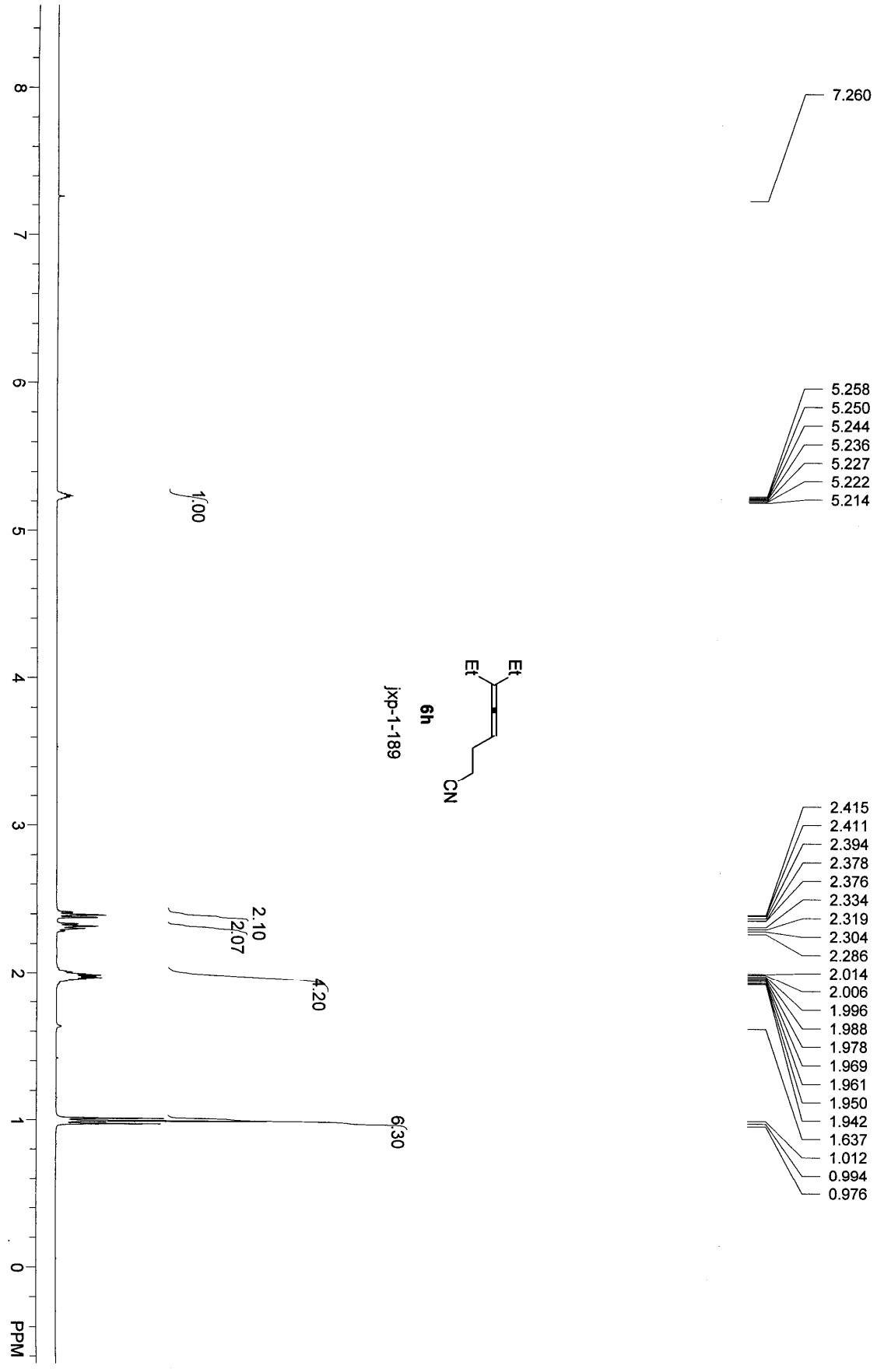

250
200
150
100
50
0
PPM
jxp-1-115-c
1f
Bu-n
COOH
204.940
179.976
102.315
77.424
77.247
77.000
76.576
32.170
32.098
29.556
26.208
22.318
13.900

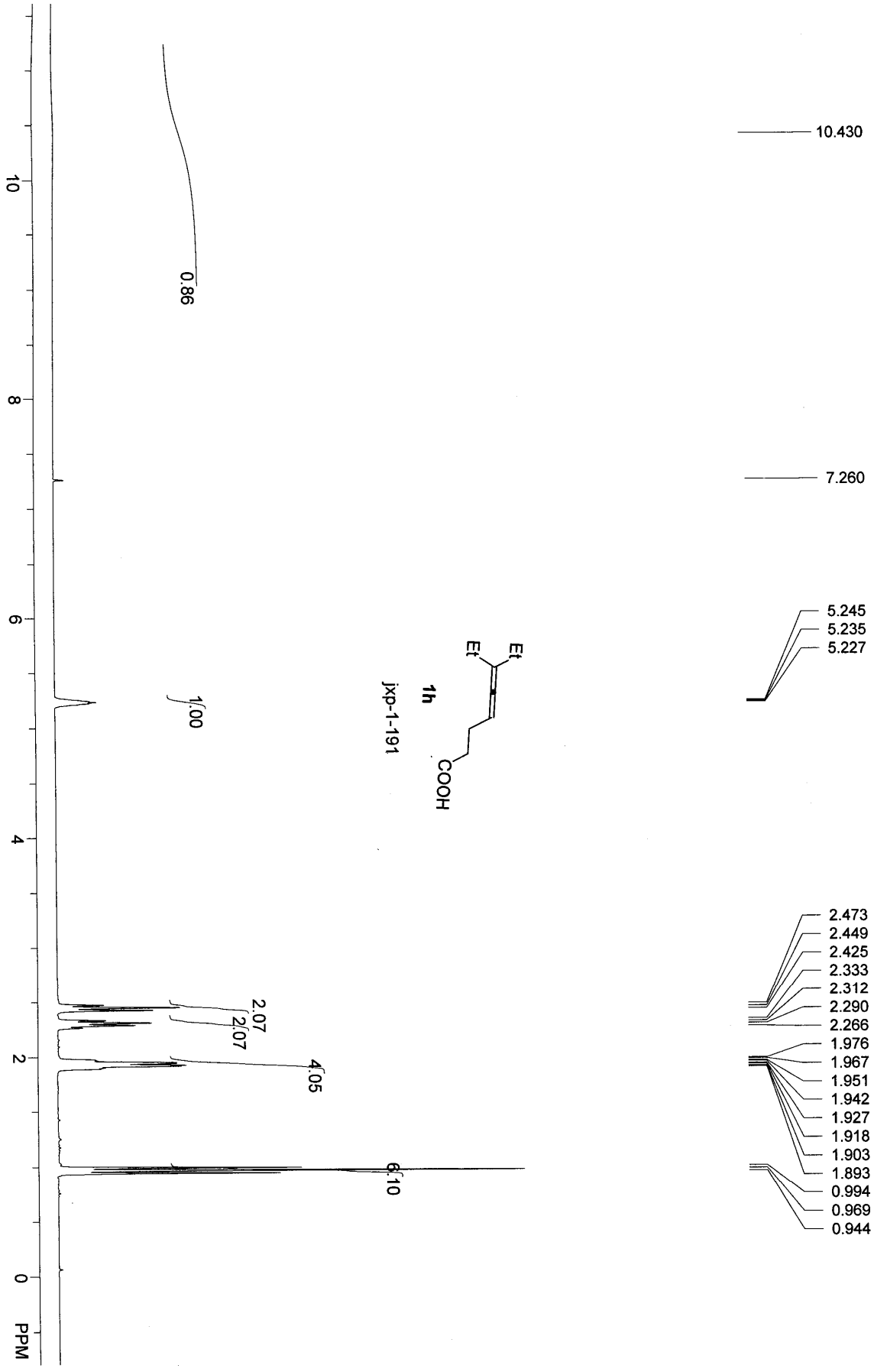

7.260
4.971
4.967
4.961
4.956
4.951
4.946
4.940
4.935
4.930
3.686
3.670
3.654
2.231
2.216
2.201
2.185
2.109
2.094
2.080
2.060
1.812
1.624
1.608
1.592
1.578
1.562
1.547
1.532
1.515
1.507
1.501
1.498
1.487
1.472
1.457
1.00
2.10
2.10
4.28
0.99
6.72
jxp-1-61
5g
OH
8
6
4
2
0
PPM

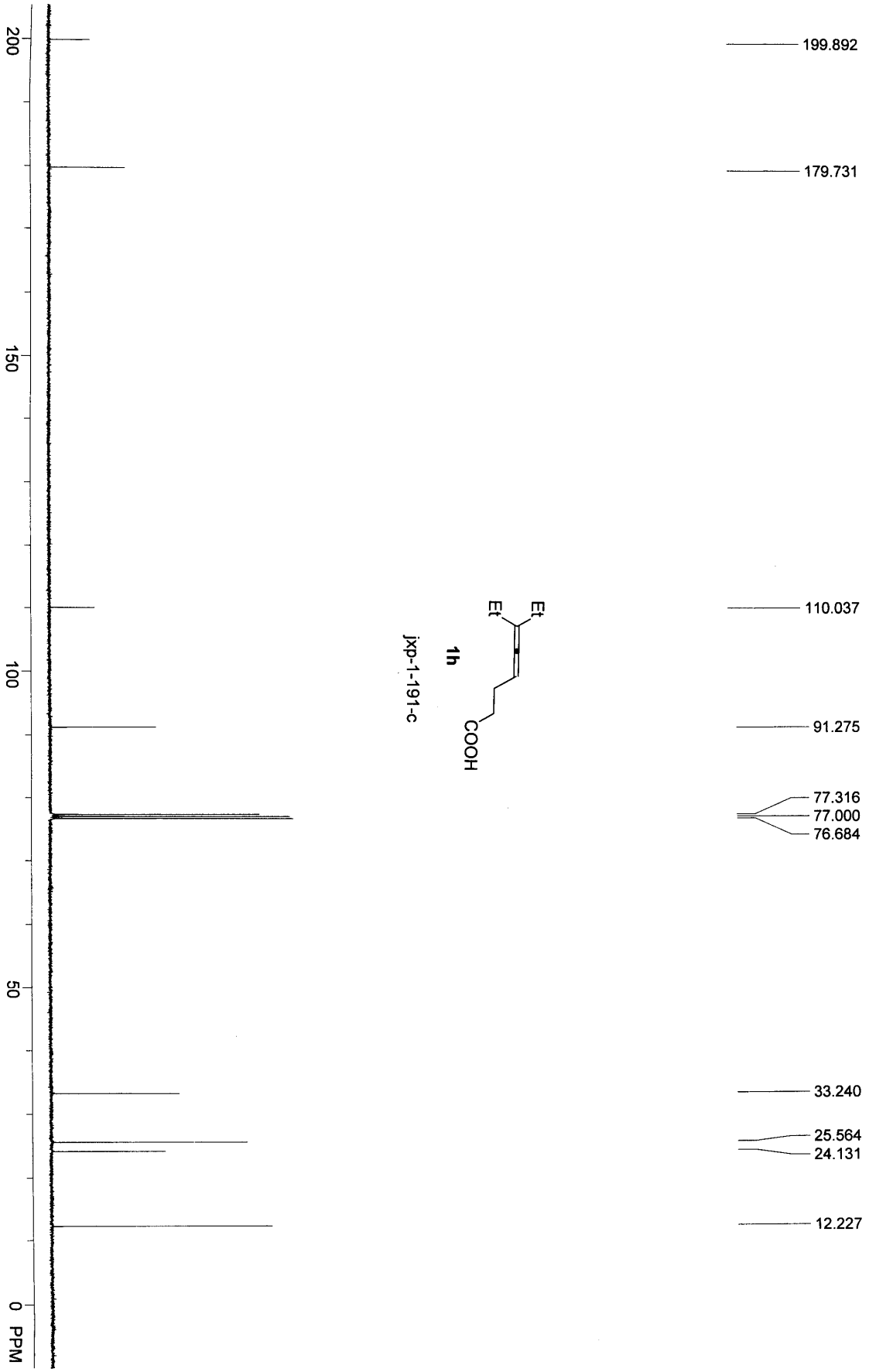

7.260
5.060
5.051
5.046
5.041
5.033
2.435
2.418
2.400
2.312
2.297
2.281
2.264
2.174
2.157
2.155
2.142
2.128
2.124
2.111
2.105
2.090
1.636
1.620
1.605
1.592
1.581
1.563
1.547
1.540
1.532
1.522
1.506
1.494
jxp-1-66
6g
CN
1.00
2.24
2.17
4.23
4.59
2.42
PPM

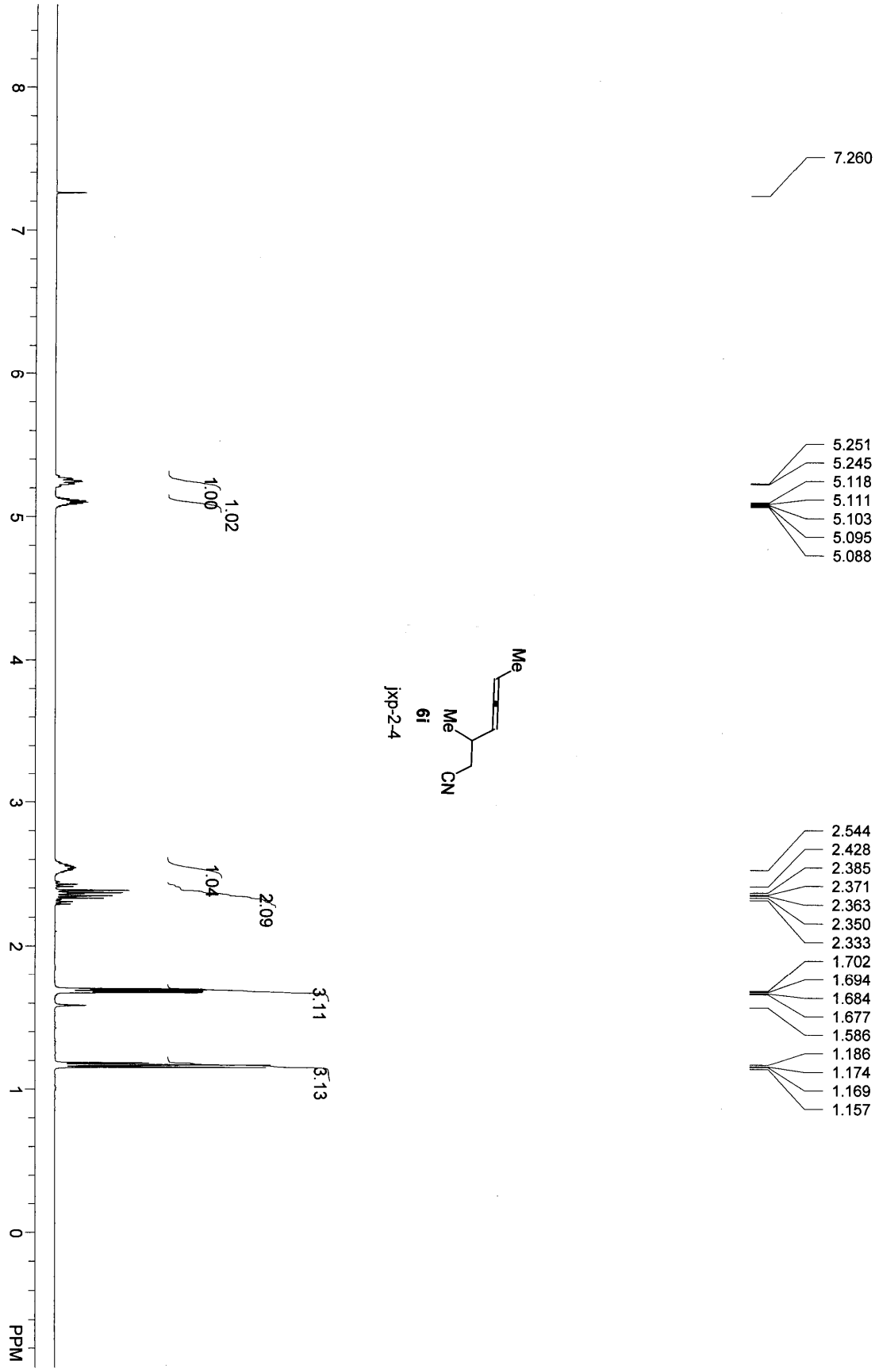

14
12
10
8
6
4
2
0
PPM
0.48
1.00
2.09
2.13
4.17
6.32
jxp-1-67
1g
COOH
11.237
7.260
5.047
5.042
5.037
5.029
2.480
2.463
2.445
2.300
2.282
2.268
2.250
2.089
2.075
2.064
2.060
1.581
1.568
1.555
1.537
1.526
1.519
1.512
1.502
1.485

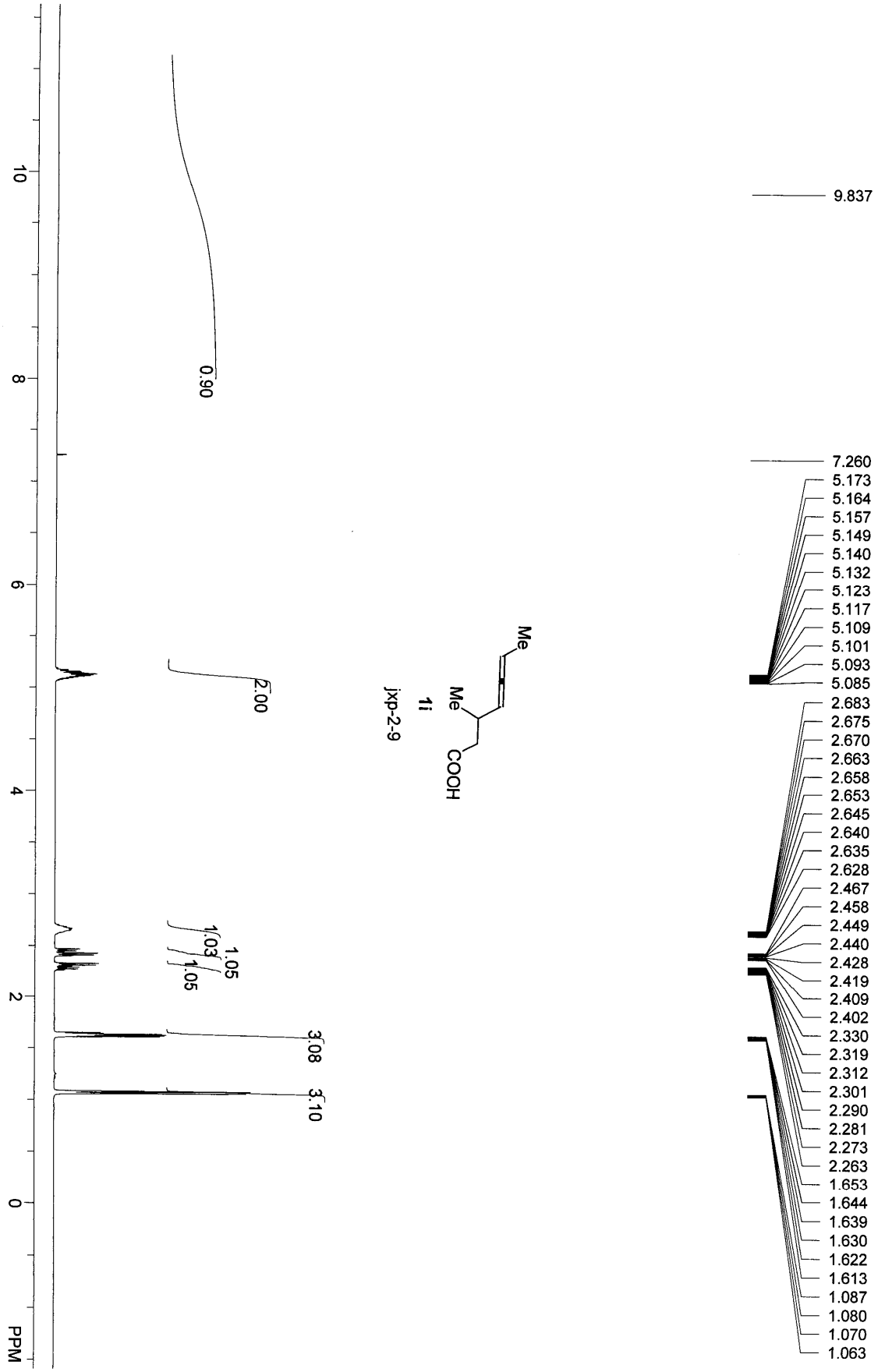

250
200
150
100
50
0
PPM
198.086
179.751
104.494
87.100
77.323
77.000
76.685
32.985
31.540
27.310
26.075
23.819
jxp-1-67-c
1g
COOH


7.260
5.258
5.250
5.244
5.236
5.227
5.222
5.214
2.415
2.411
2.394
2.378
2.376
2.334
2.319
2.304
2.286
2.014
2.006
1.996
1.988
1.978
1.969
1.961
1.950
1.942
1.637
1.012
0.994
0.976
Et
Et
CN
6h
jxp-1-189
1.00
2.10
2.07
4.20
6.30
PPM

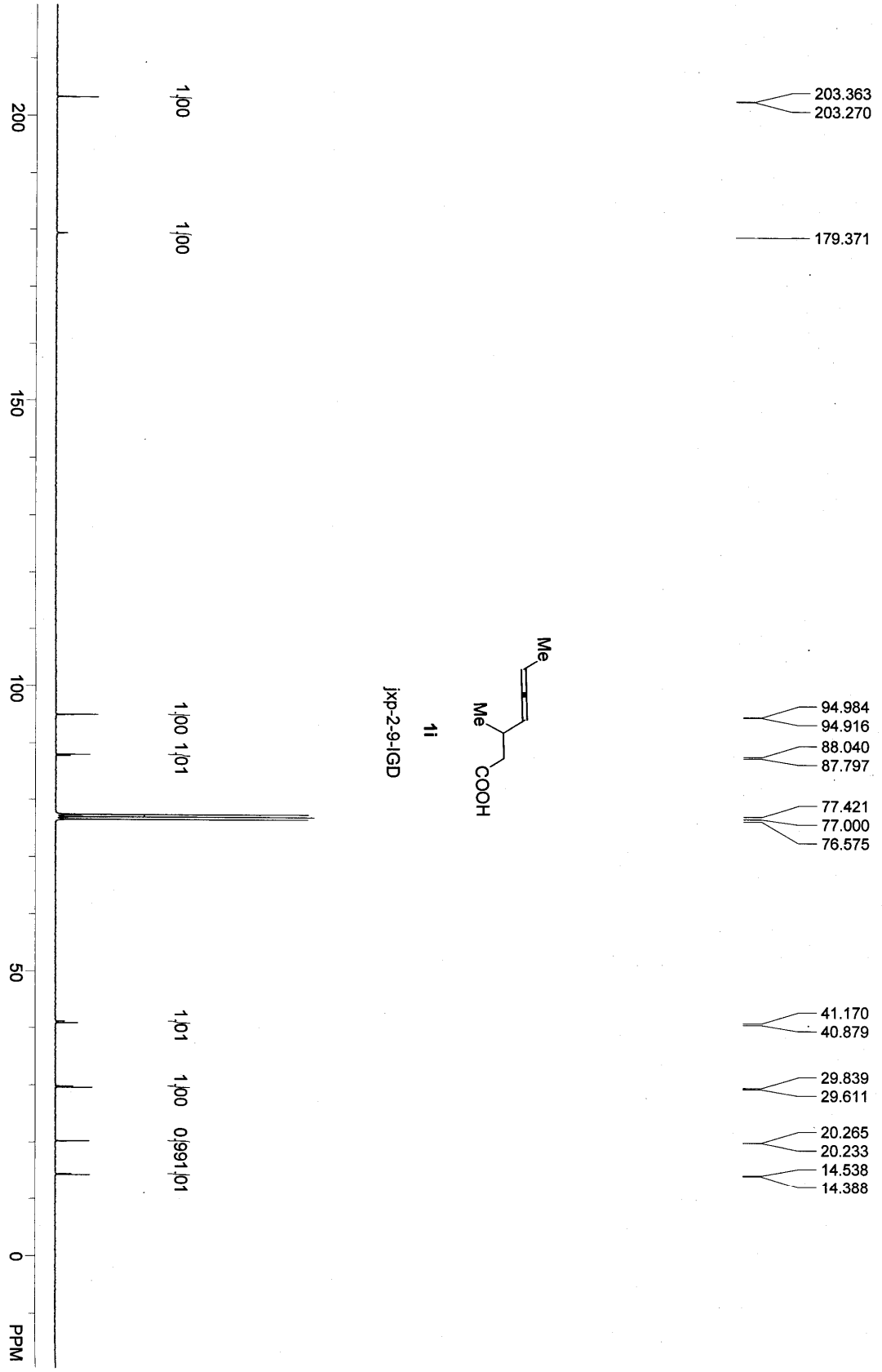

10.430
7.260
5.245
5.235
5.227
2.473
2.449
2.425
2.333
2.312
2.290
2.266
1.976
1.967
1.951
1.942
1.927
1.918
1.903
1.893
0.994
0.969
0.944
Et
Et
1h
jxp-1-191
COOH
0.86
1.00
2.07
2.07
4.05
6.10
10
8
6
4
2
0
PPM

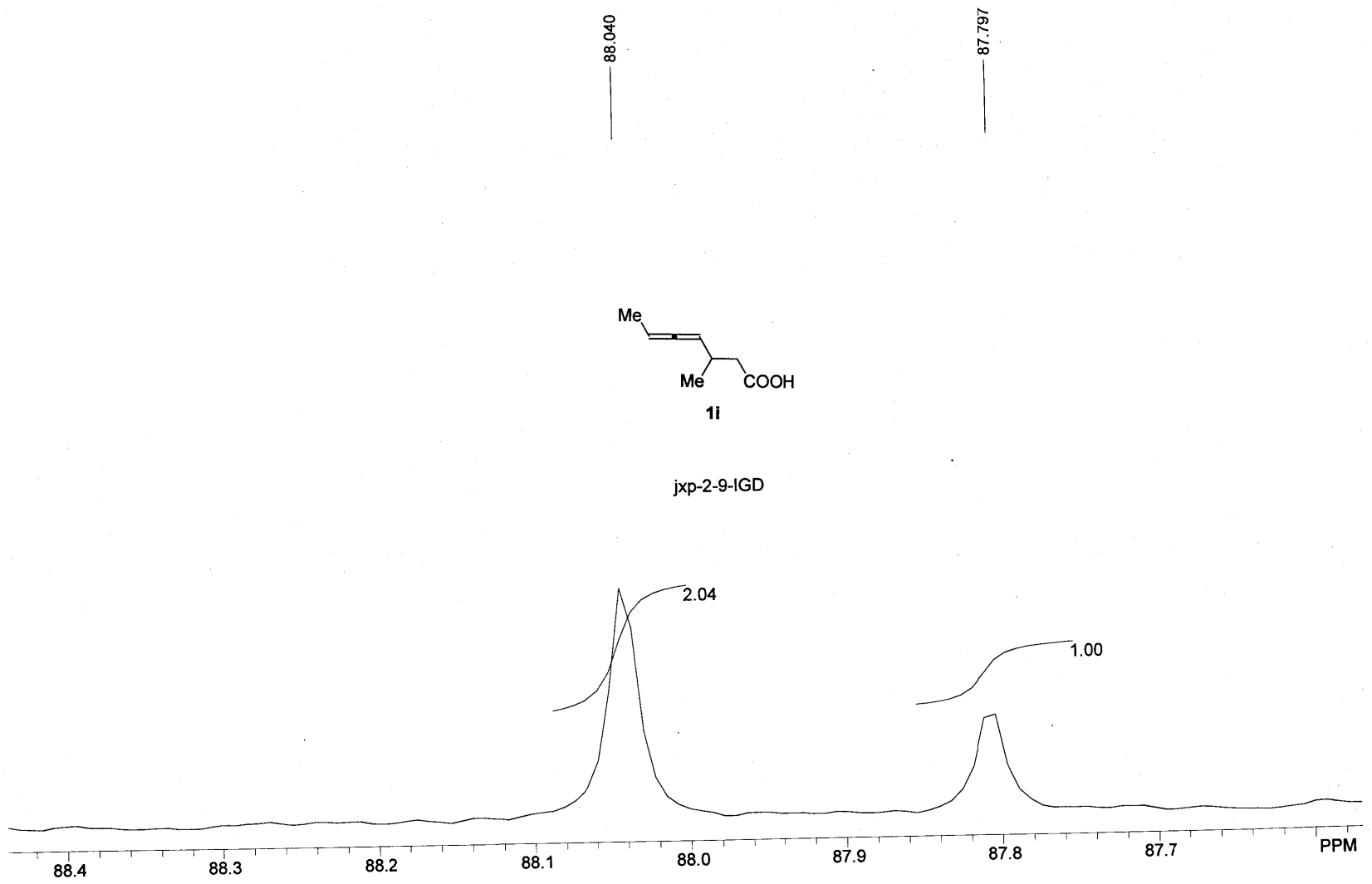

199.892
179.731
110.037
91.275
77.316
77.000
76.684
33.240
25.564
24.131
12.227
200
150
100
50
0 PPM
Et
Et
COOH
1h
jxp-1-191-c

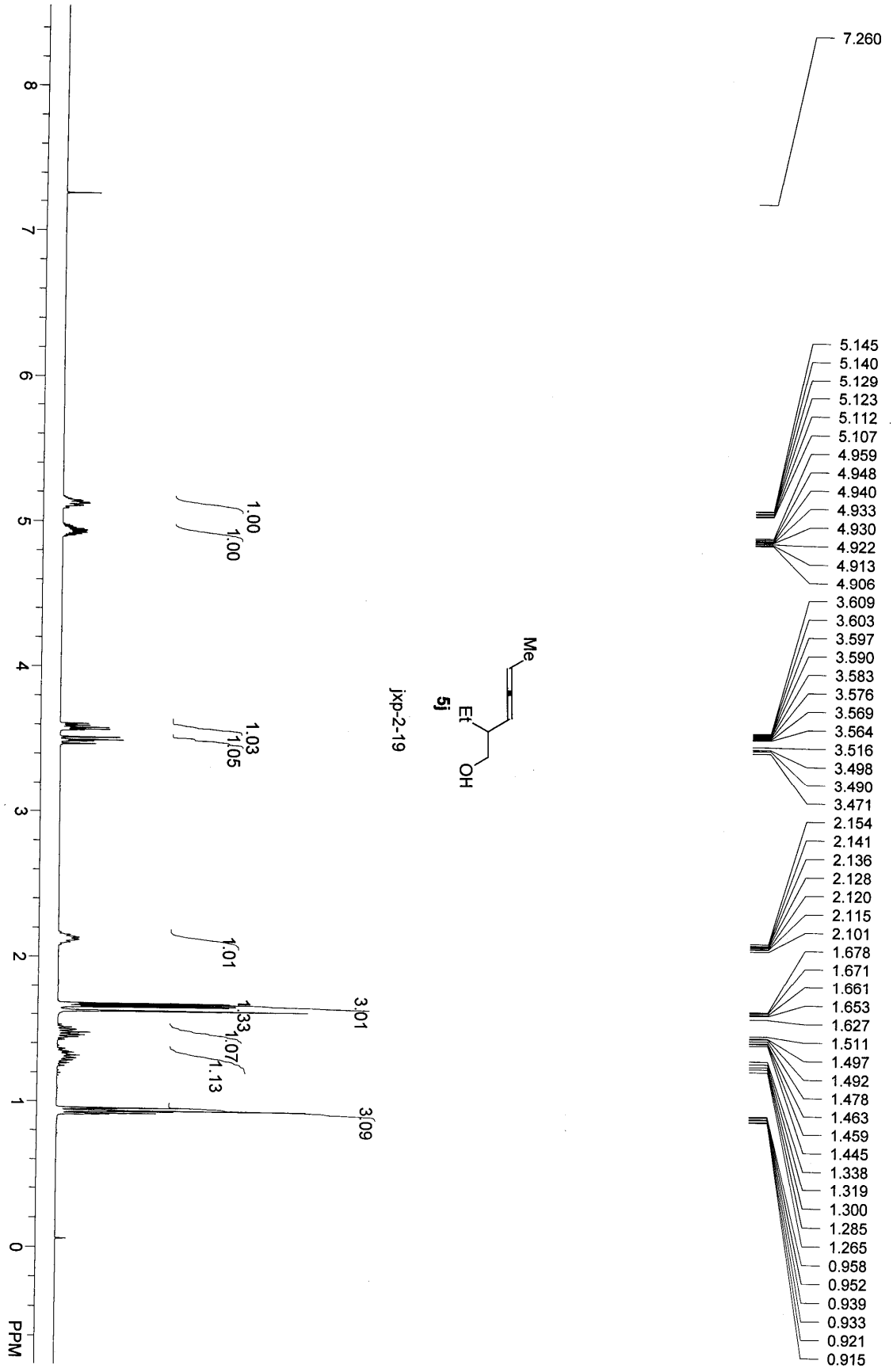

7.260
5.251
5.245
5.118
5.111
5.103
5.095
5.088
2.544
2.428
2.385
2.371
2.363
2.350
2.333
1.702
1.694
1.684
1.677
1.586
1.186
1.174
1.169
1.157
Me
Me
CN
6i
jxp-2-4
1.00
1.02
1.04
2.09
3.11
3.13
PPM

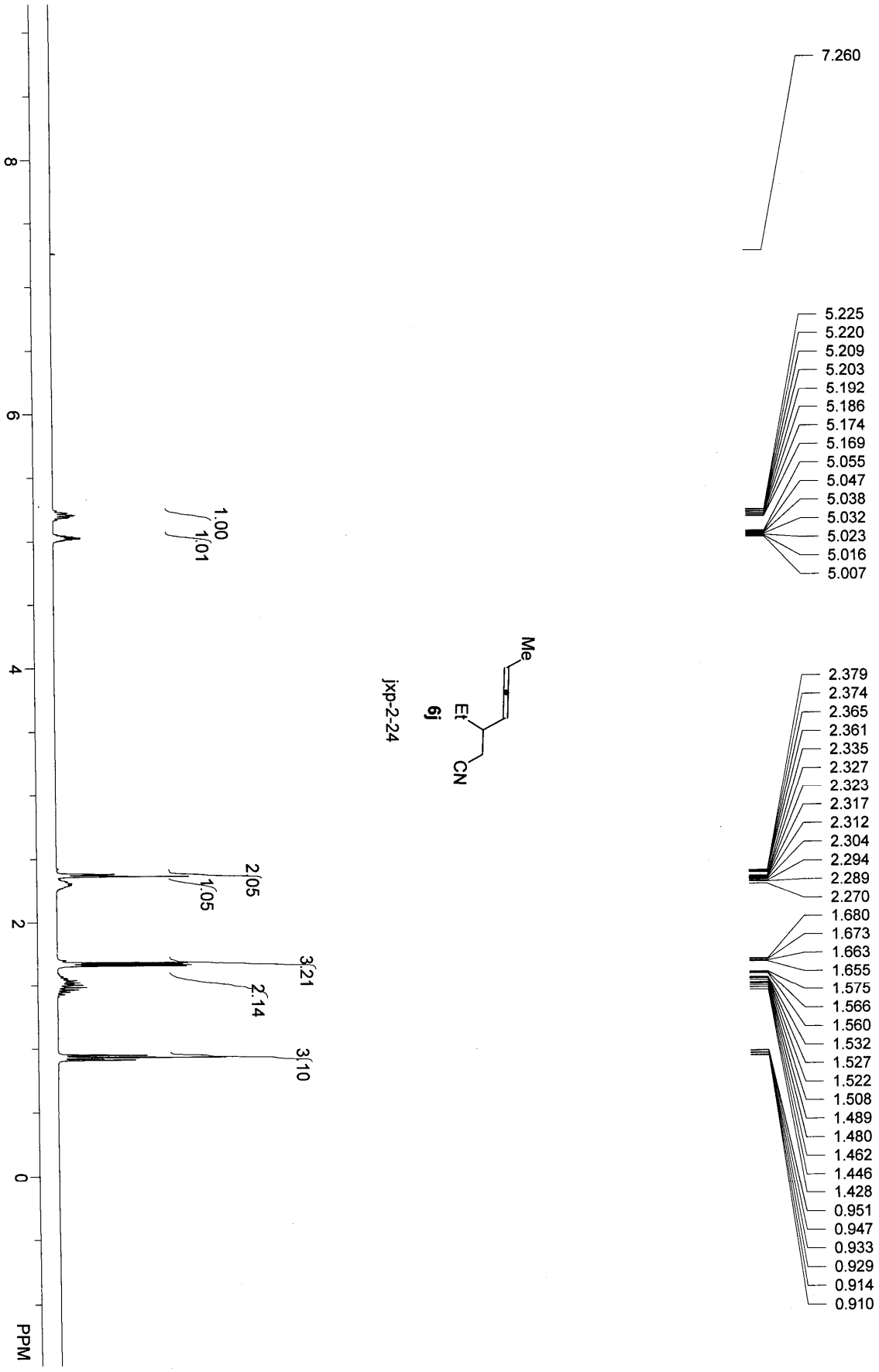

9.837
7.260
5.173
5.164
5.157
5.149
5.140
5.132
5.123
5.117
5.109
5.101
5.093
5.085
2.683
2.675
2.670
2.663
2.658
2.653
2.645
2.640
2.635
2.628
2.467
2.458
2.449
2.440
2.428
2.419
2.409
2.402
2.330
2.319
2.312
2.301
2.290
2.281
2.273
2.263
1.653
1.644
1.639
1.630
1.622
1.613
1.087
1.080
1.070
1.063
Me
Me
COOH
1i
jxp-2-9
0.90
2.00
1.05
1.03
1.05
3.08
3.10
10
8
6
4
2
0
PPM

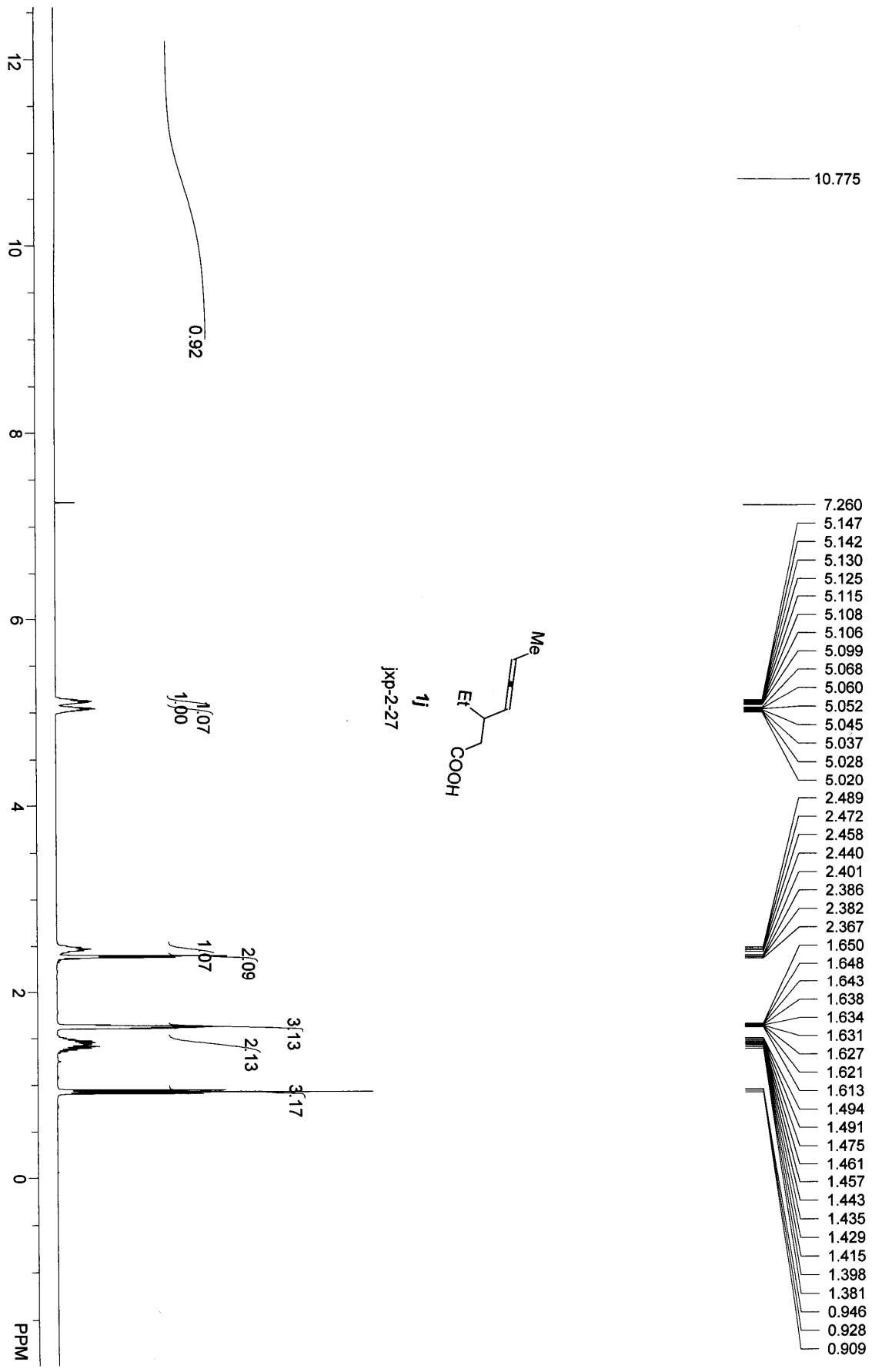
Inverse gated decoupling ^{13}C NMR analysis for the determination of the *dr* value of **1i.**



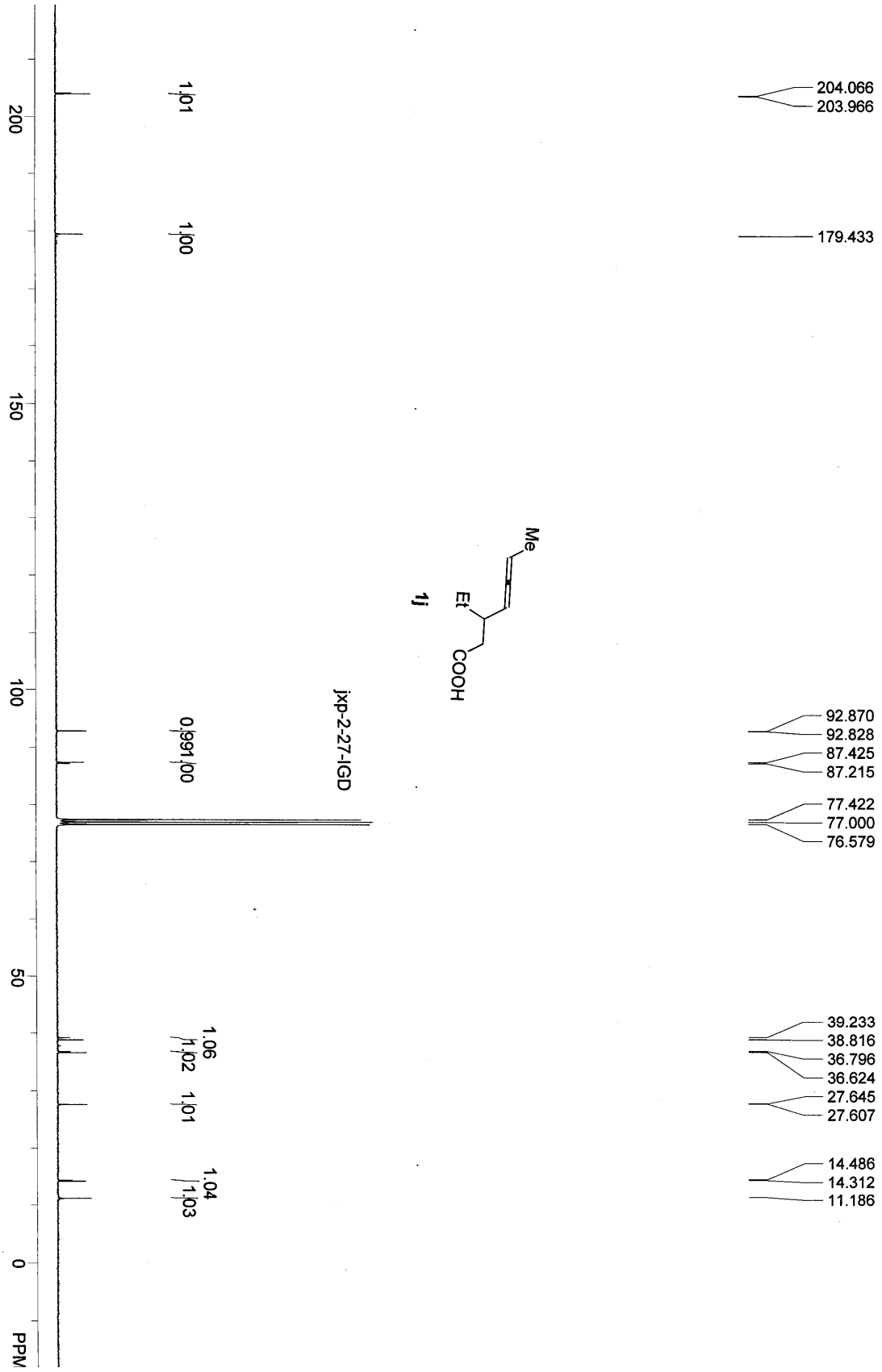

88.040
87.797
Me
Me
COOH
1i
jxp-2-9-IGD
2.04
1.00
88.4
88.3
88.2
88.1
88.0
87.9
87.8
87.7
PPM

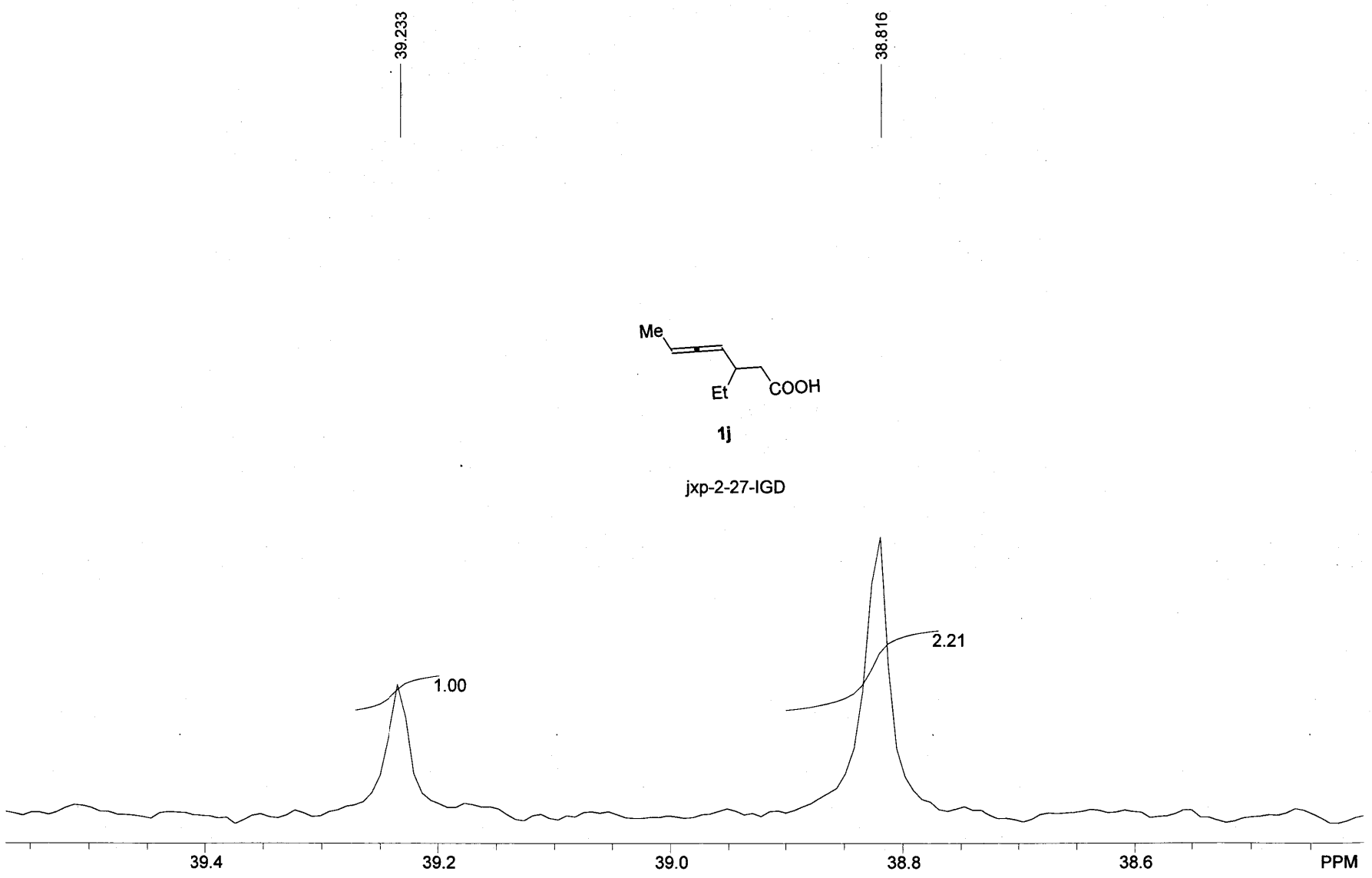

7.260
5.145
5.140
5.129
5.123
5.112
5.107
4.959
4.948
4.940
4.933
4.930
4.922
4.913
4.906
3.609
3.603
3.597
3.590
3.583
3.576
3.569
3.564
3.516
3.498
3.490
3.471
2.154
2.141
2.136
2.128
2.120
2.115
2.101
1.678
1.671
1.661
1.653
1.627
1.511
1.497
1.492
1.478
1.463
1.459
1.445
1.338
1.319
1.300
1.285
1.265
0.958
0.952
0.939
0.933
0.921
0.915
Me
Et
OH
5j
jxp-2-19
1.00
1.00
1.03
1.05
1.01
3.01
1.33
1.07
1.13
3.09
PPM

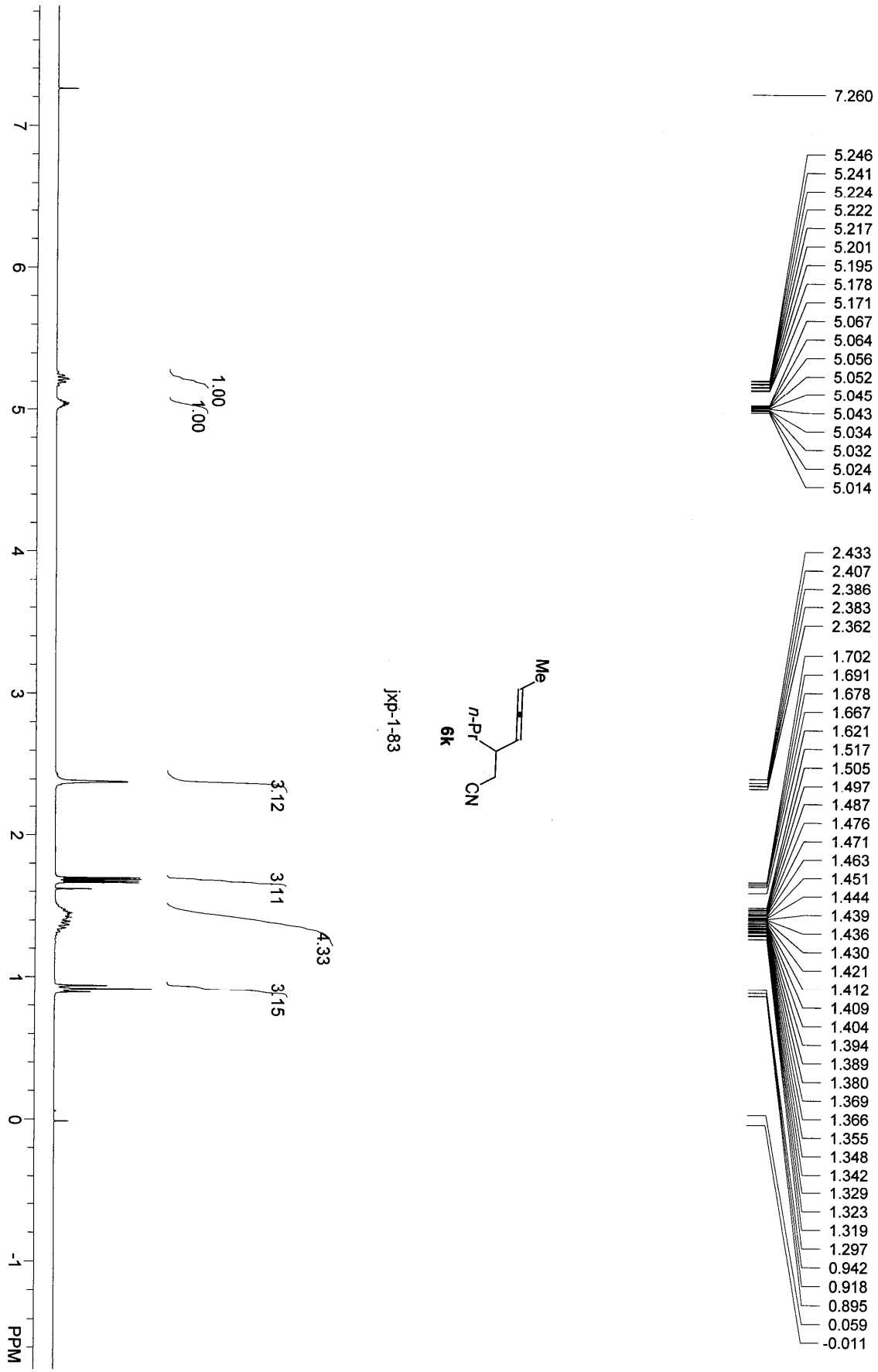

7.260
5.225
5.220
5.209
5.203
5.192
5.186
5.174
5.169
5.055
5.047
5.038
5.032
5.023
5.016
5.007
2.379
2.374
2.365
2.361
2.335
2.327
2.323
2.317
2.312
2.304
2.294
2.289
2.270
1.680
1.673
1.663
1.655
1.575
1.566
1.560
1.532
1.527
1.522
1.508
1.489
1.480
1.462
1.446
1.428
0.951
0.947
0.933
0.929
0.914
0.910
Me
Et
CN
6j
jxp-2-24
1.00
1.01
2.05
1.05
3.21
2.14
3.10
8
6
4
2
0
PPM

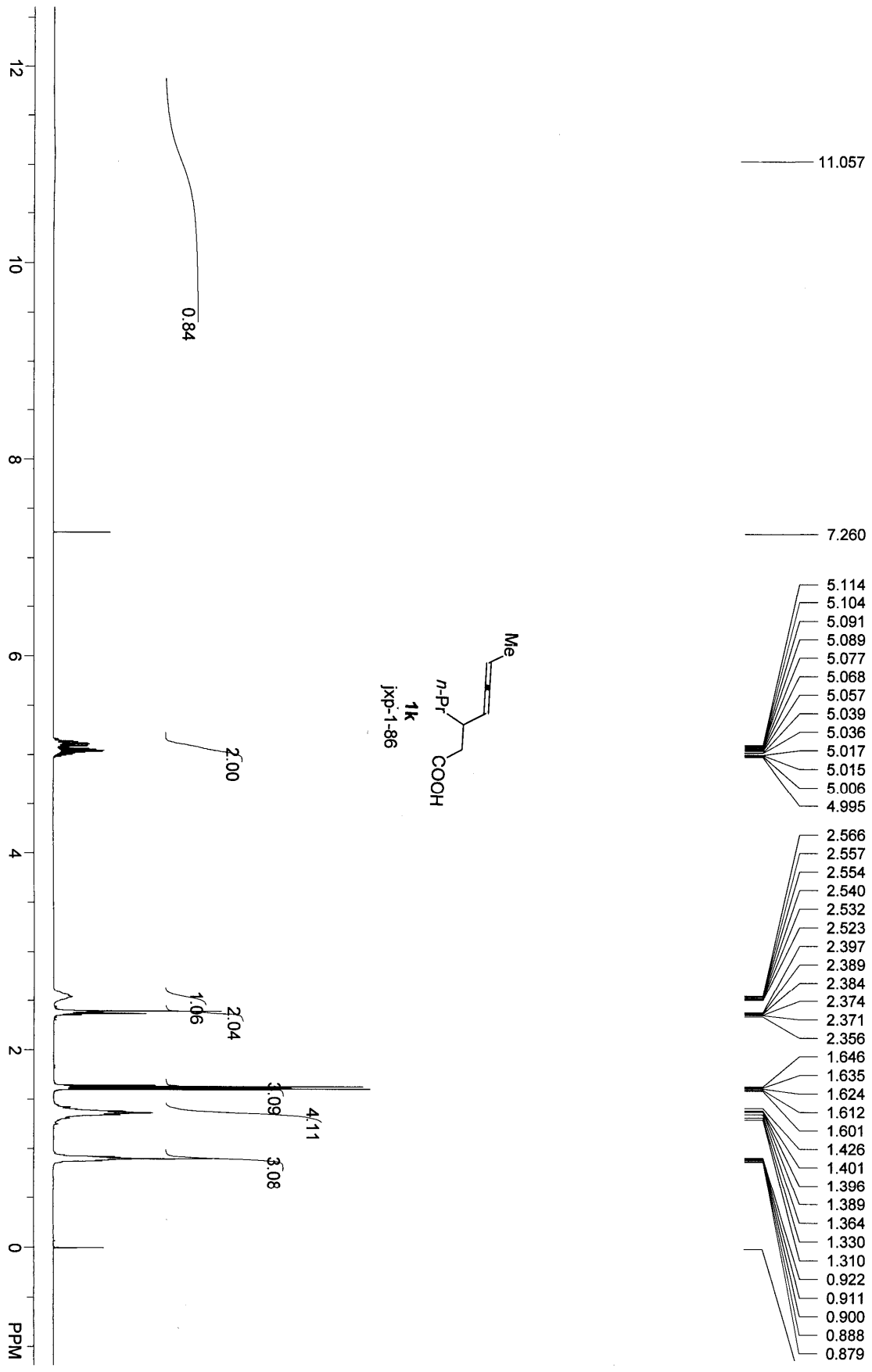

10.775
7.260
5.147
5.142
5.130
5.125
5.115
5.108
5.106
5.099
5.068
5.060
5.052
5.045
5.037
5.028
5.020
2.489
2.472
2.458
2.440
2.401
2.386
2.382
2.367
1.650
1.648
1.643
1.638
1.634
1.631
1.627
1.621
1.613
1.494
1.491
1.475
1.461
1.457
1.443
1.435
1.429
1.415
1.398
1.381
0.946
0.928
0.909
Me
Et
COOH
1j
jxp-2-27
0.92
1.07
1.00
1.07
2.09
3.13
2.13
3.17
12
10
8
6
4
2
0
PPM

Inverse gated decoupling ^{13}C NMR analysis for the determination of the *dr* value of **1j.**

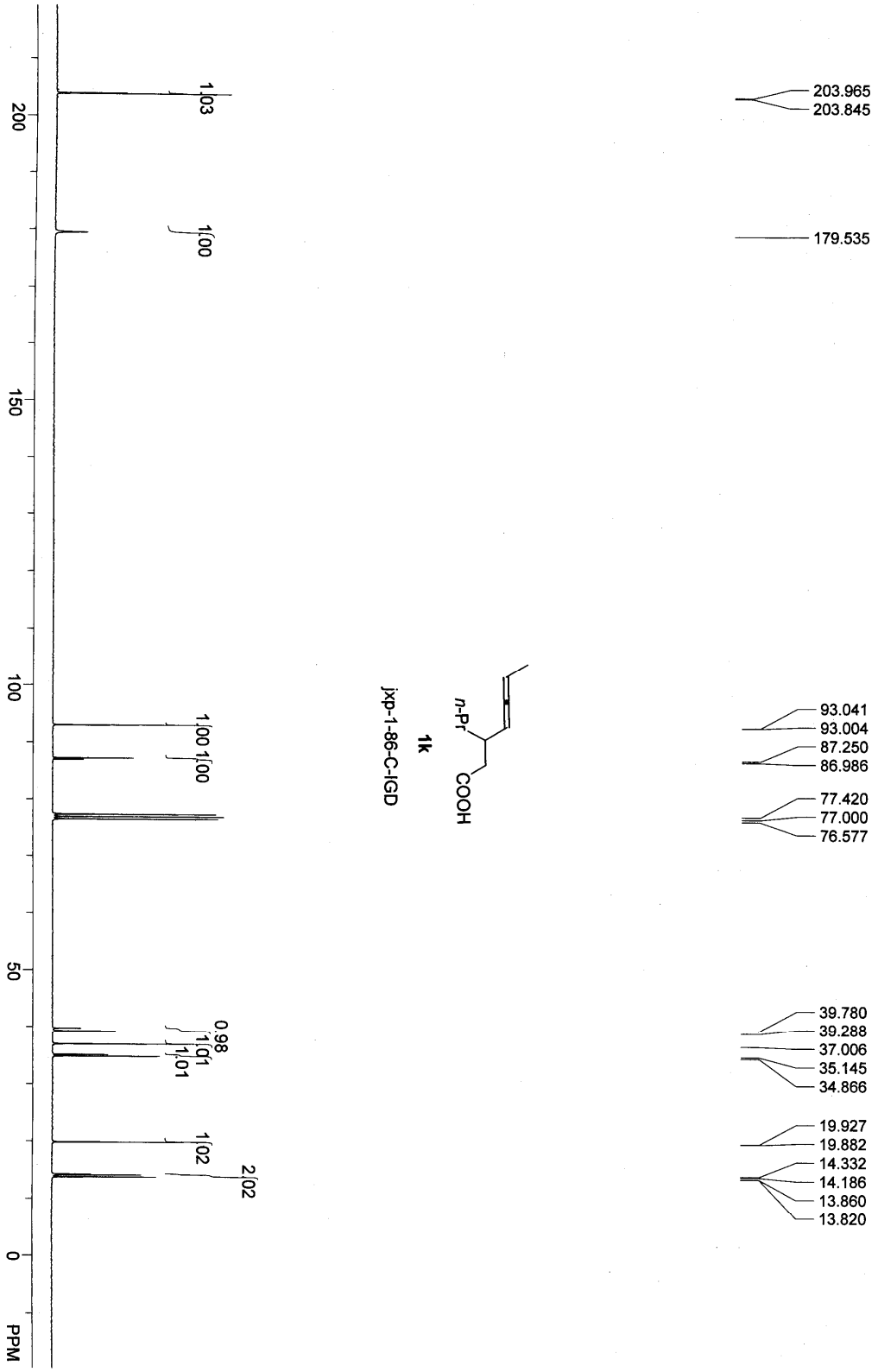


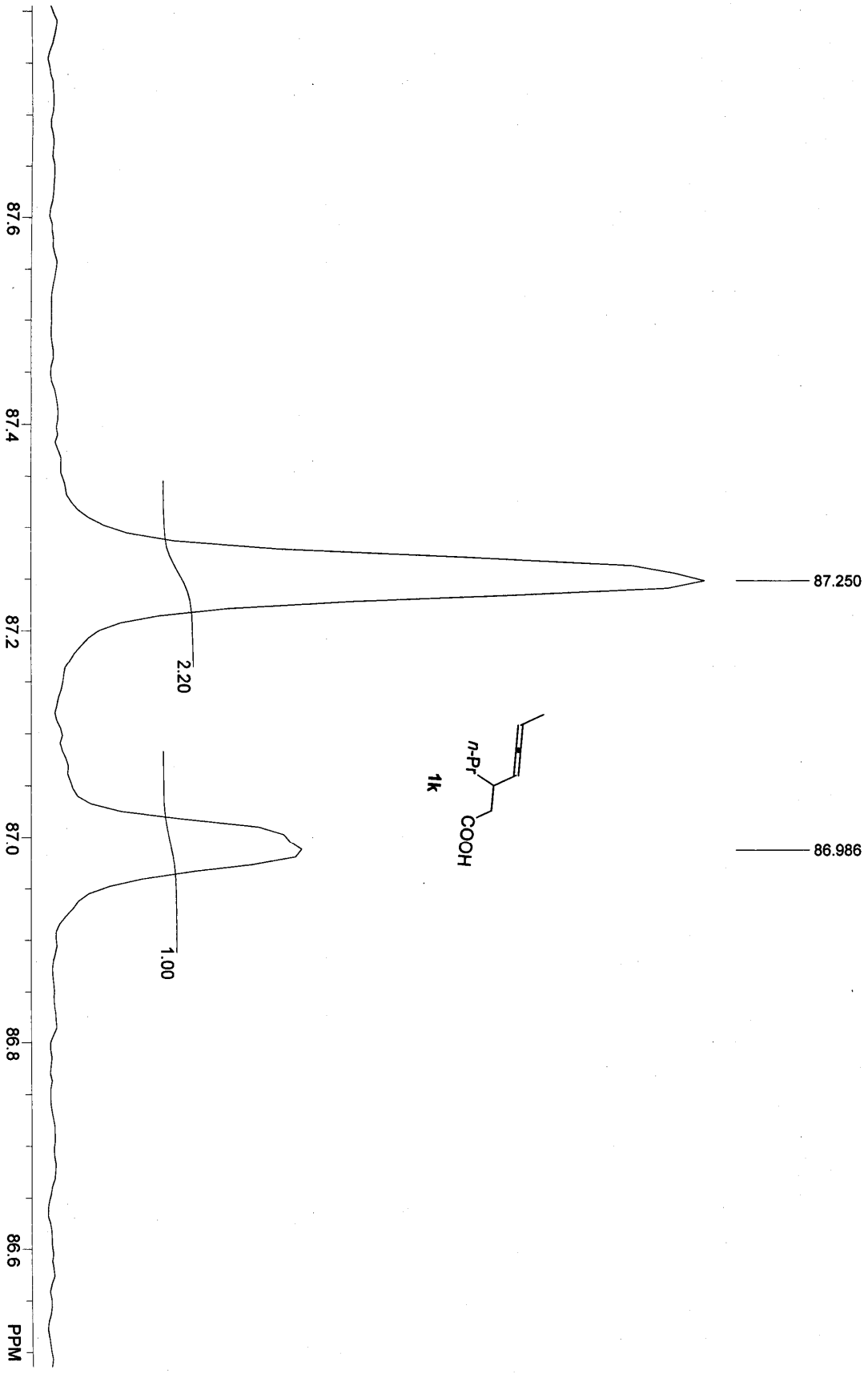

39.233
38.816
Me
Et
COOH
1j
jxp-2-27-IGD
1.00
2.21
39.4
39.2
39.0
38.8
38.6
PPM

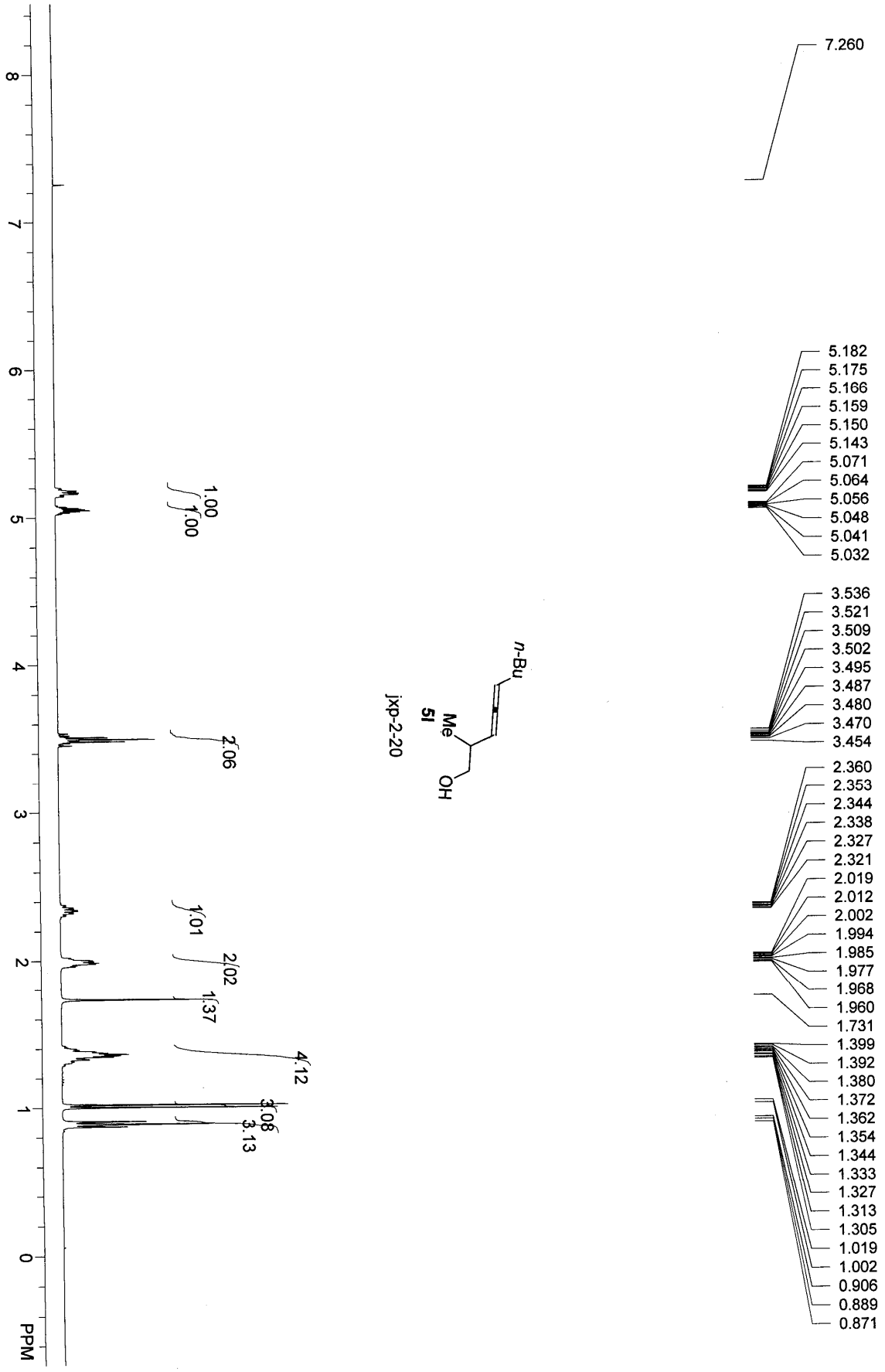

7.260
5.246
5.241
5.224
5.222
5.217
5.201
5.195
5.178
5.171
5.067
5.064
5.056
5.052
5.045
5.043
5.034
5.032
5.024
5.014
2.433
2.407
2.386
2.383
2.362
1.702
1.691
1.678
1.667
1.621
1.517
1.505
1.497
1.487
1.476
1.471
1.463
1.451
1.444
1.439
1.436
1.430
1.421
1.412
1.409
1.404
1.394
1.389
1.380
1.369
1.366
1.355
1.348
1.342
1.329
1.323
1.319
1.297
0.942
0.918
0.895
0.059
-0.011
Me
n-Pr
CN
6k
jxp-1-83
1.00
1.00
3.12
3.11
4.33
3.15
7
6
5
4
3
2
1
0
-1
PPM

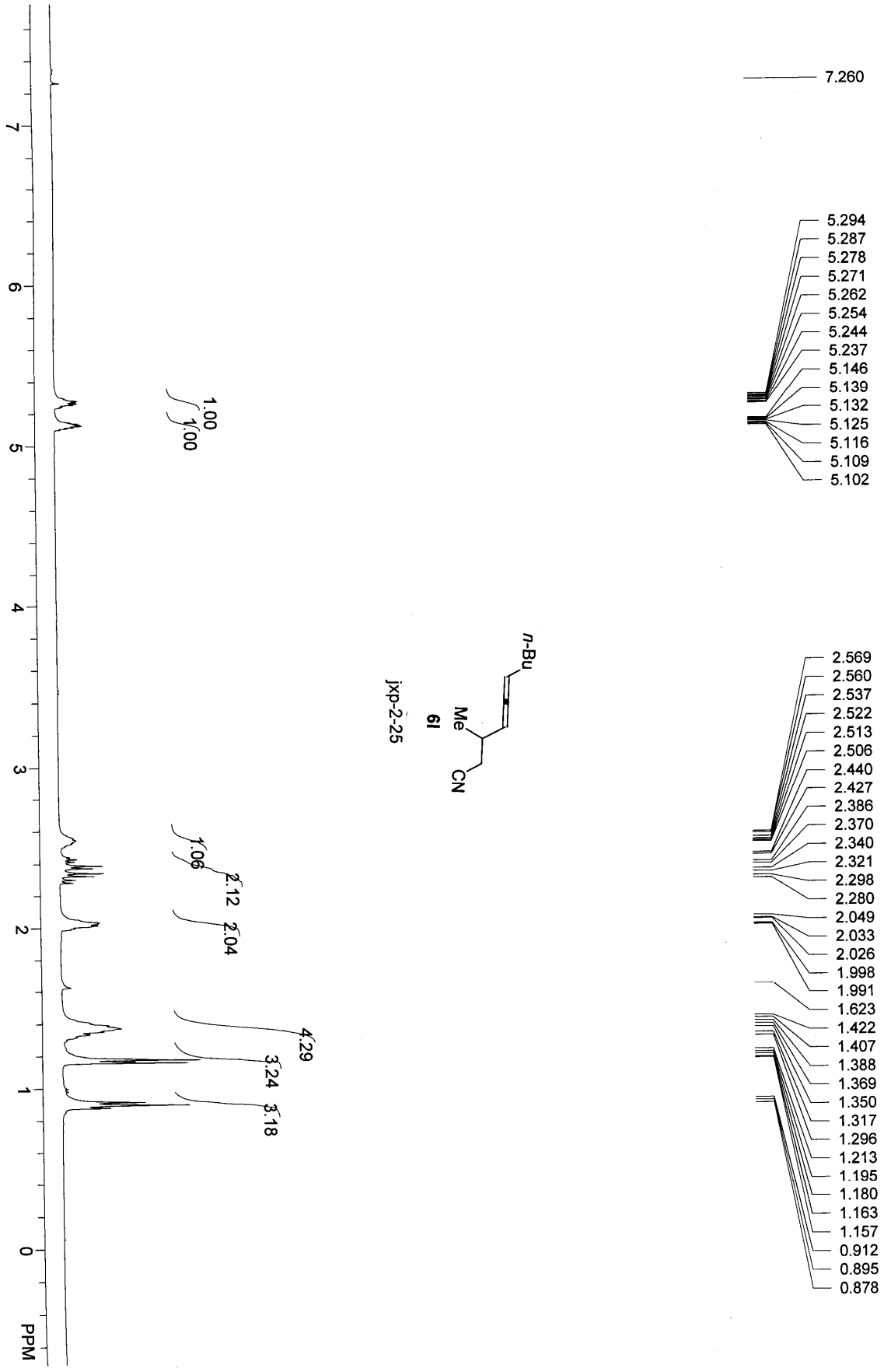

11.057
7.260
5.114
5.104
5.091
5.089
5.077
5.068
5.057
5.039
5.036
5.017
5.015
5.006
4.995
2.566
2.557
2.554
2.540
2.532
2.523
2.397
2.389
2.384
2.374
2.371
2.356
1.646
1.635
1.624
1.612
1.601
1.426
1.401
1.396
1.389
1.364
1.330
1.310
0.922
0.911
0.900
0.888
0.879
Me
n-Pr
COOH
1k
jxp-1-86
0.84
2.00
1.06
2.04
3.09
4.11
3.08
12
10
8
6
4
2
0
PPM

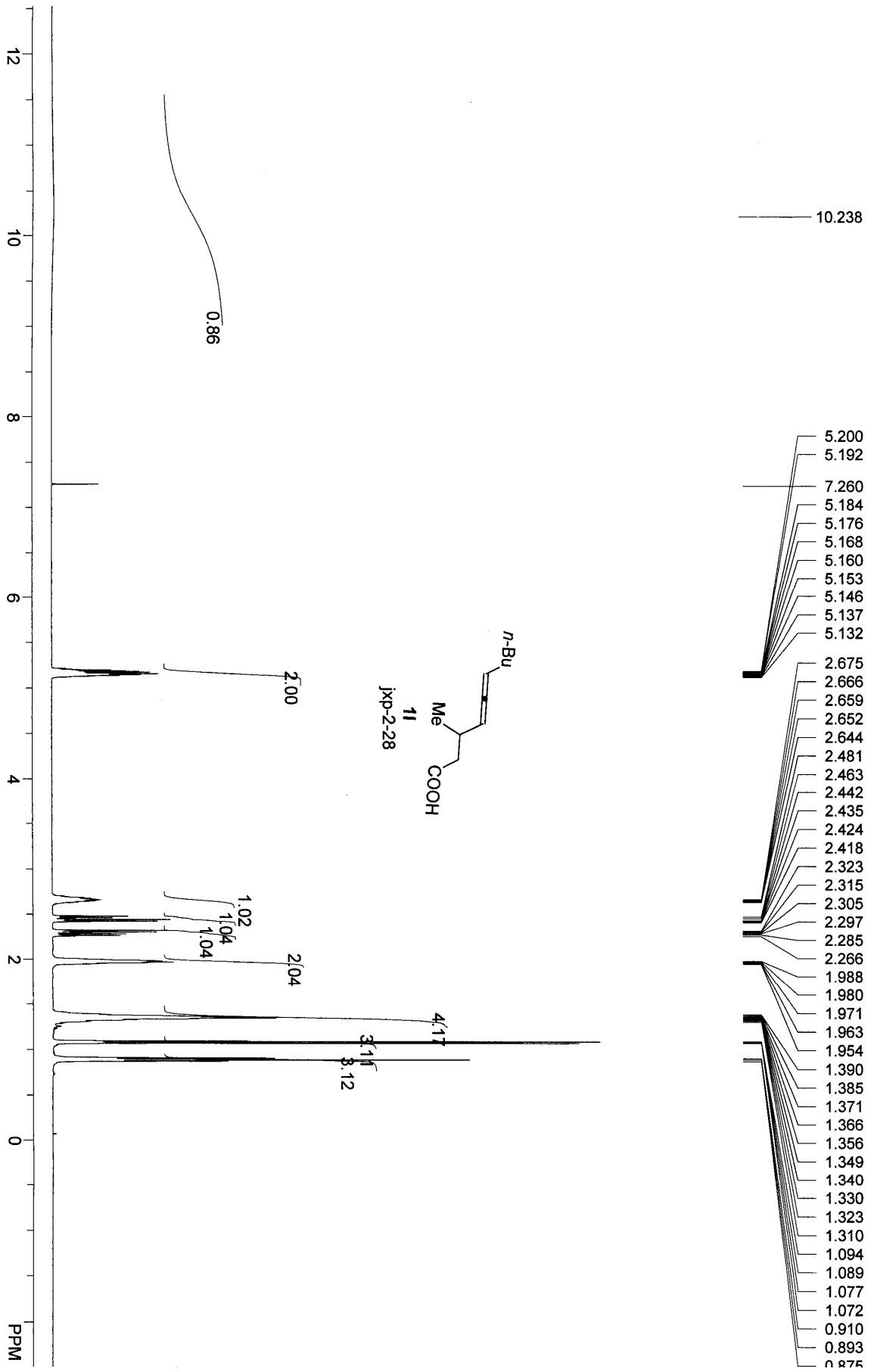
Inverse gated decoupling ^{13}C NMR analysis for the determination of the *dr* value of **1k.**




87.6
87.4
87.2
87.0
86.8
86.6
PPM
2.20
1.00
87.250
86.986
n-Pr
COOH
1k


7.260
5.182
5.175
5.166
5.159
5.150
5.143
5.071
5.064
5.056
5.048
5.041
5.032
3.536
3.521
3.509
3.502
3.495
3.487
3.480
3.470
3.454
2.360
2.353
2.344
2.338
2.327
2.321
2.019
2.012
2.002
1.994
1.985
1.977
1.968
1.960
1.731
1.399
1.392
1.380
1.372
1.362
1.354
1.344
1.333
1.327
1.313
1.305
1.019
1.002
0.906
0.889
0.871
n-Bu
Me
5l
OH
jxp-2-20
1.00
1.00
2.06
1.01
2.02
1.37
4.12
3.08
3.13
PPM


7.260
5.294
5.287
5.278
5.271
5.262
5.254
5.244
5.237
5.146
5.139
5.132
5.125
5.116
5.109
5.102
n-Bu
Me
CN
6l
jxp-2-25
2.569
2.560
2.537
2.522
2.513
2.506
2.440
2.427
2.386
2.370
2.340
2.321
2.298
2.280
2.049
2.033
2.026
1.998
1.991
1.623
1.422
1.407
1.388
1.369
1.350
1.317
1.296
1.213
1.195
1.180
1.163
1.157
0.912
0.895
0.878
1.00
1.00
1.06
2.12
2.04
4.29
3.24
3.18
PPM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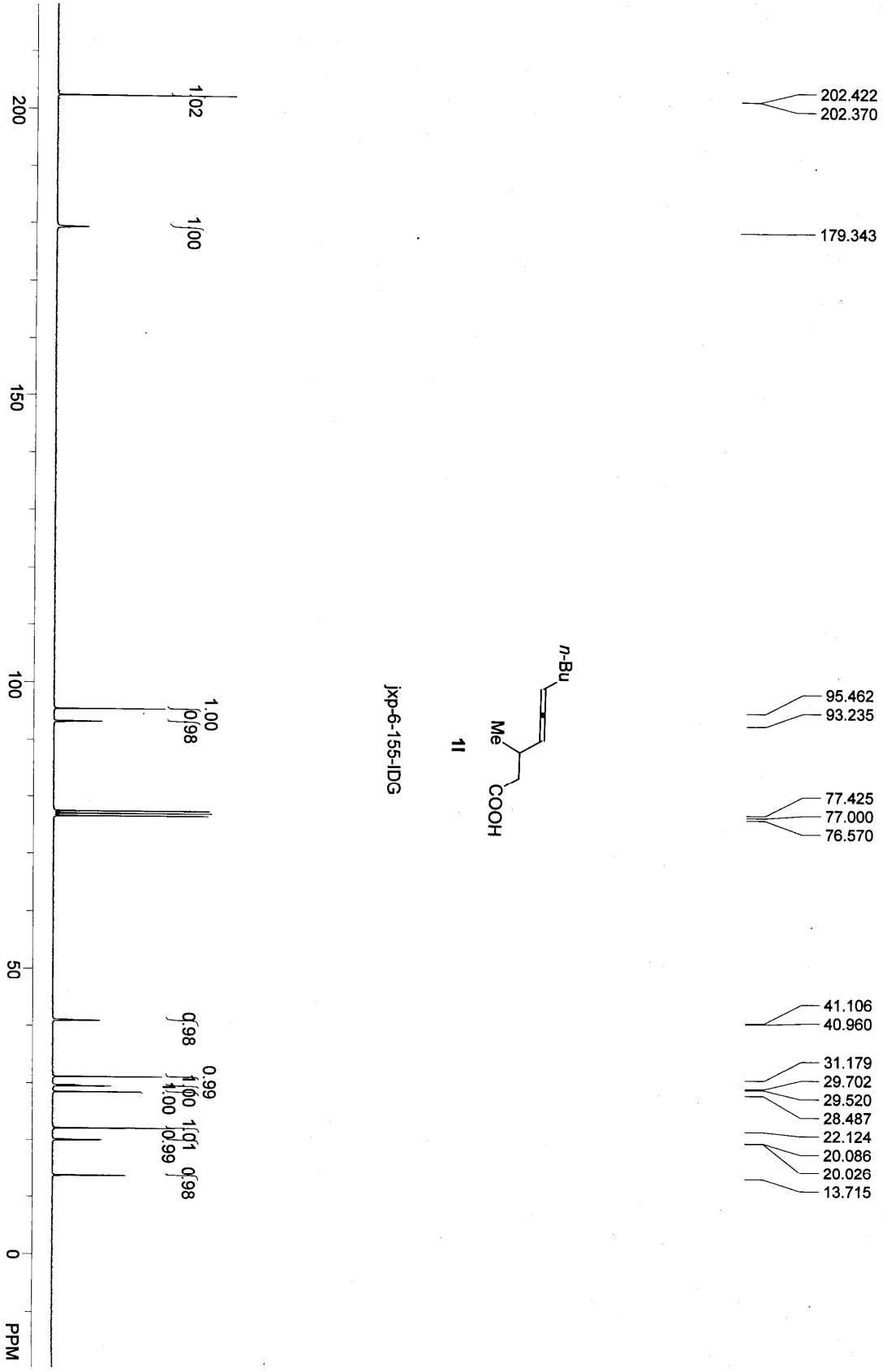
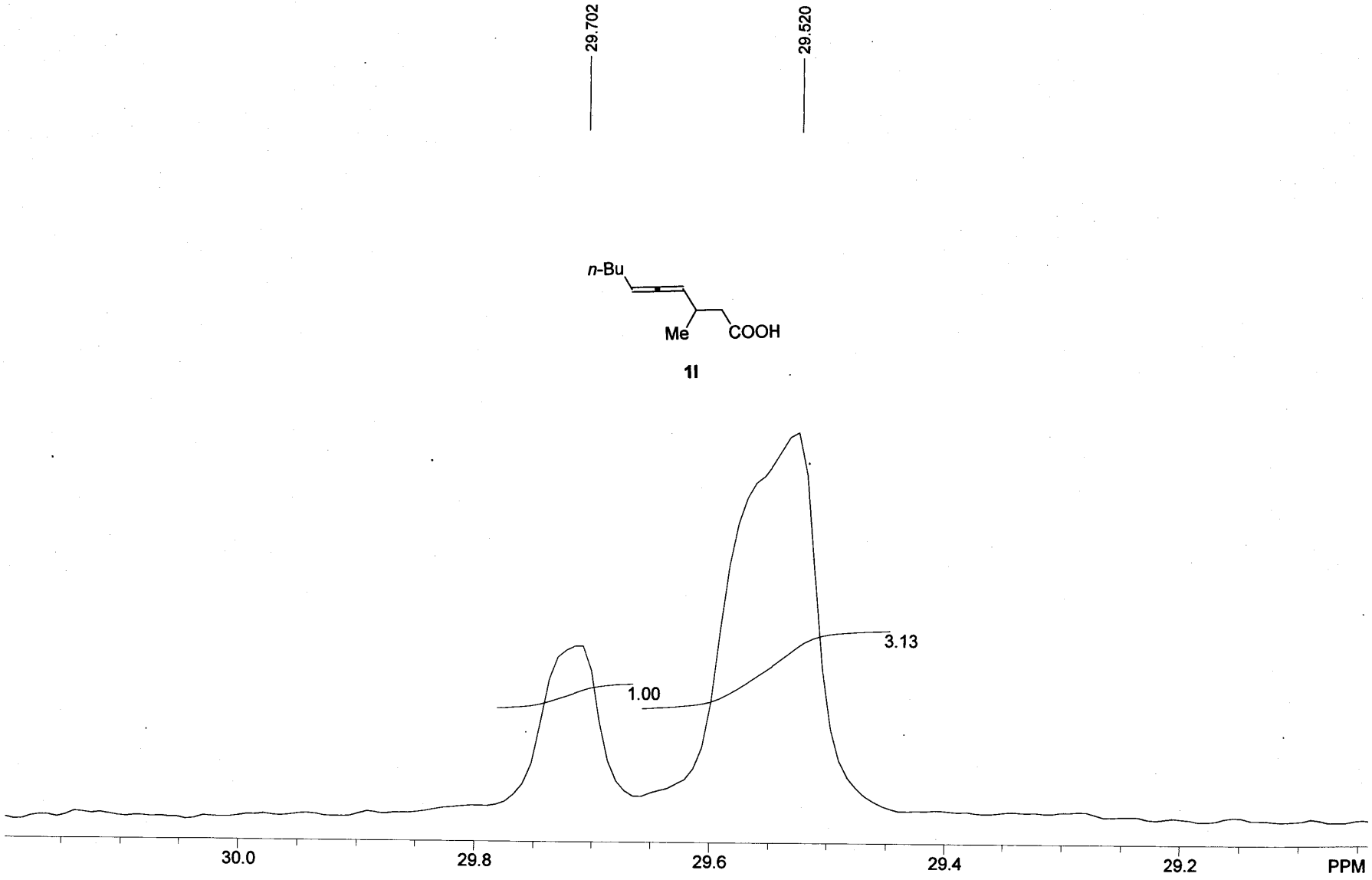
10
8
6
4
2
0
PPM
0.86
2.00
1.02
1.04
1.04
2.04
4.17
3.11
3.12
n-Bu
Me
COOH
1l
jxp-2-28
10.238
5.200
5.192
7.260
5.184
5.176
5.168
5.160
5.153
5.146
5.137
5.132
2.675
2.666
2.659
2.652
2.644
2.481
2.463
2.442
2.435
2.424
2.418
2.323
2.315
2.305
2.297
2.285
2.266
1.988
1.980
1.971
1.963
1.954
1.390
1.385
1.371
1.366
1.356
1.349
1.340
1.330
1.323
1.310
1.094
1.089
1.077
1.072
0.910
0.893

Inverse gated decoupling ^{13}C NMR analysis for the determination of the *dr* value of **1l.**

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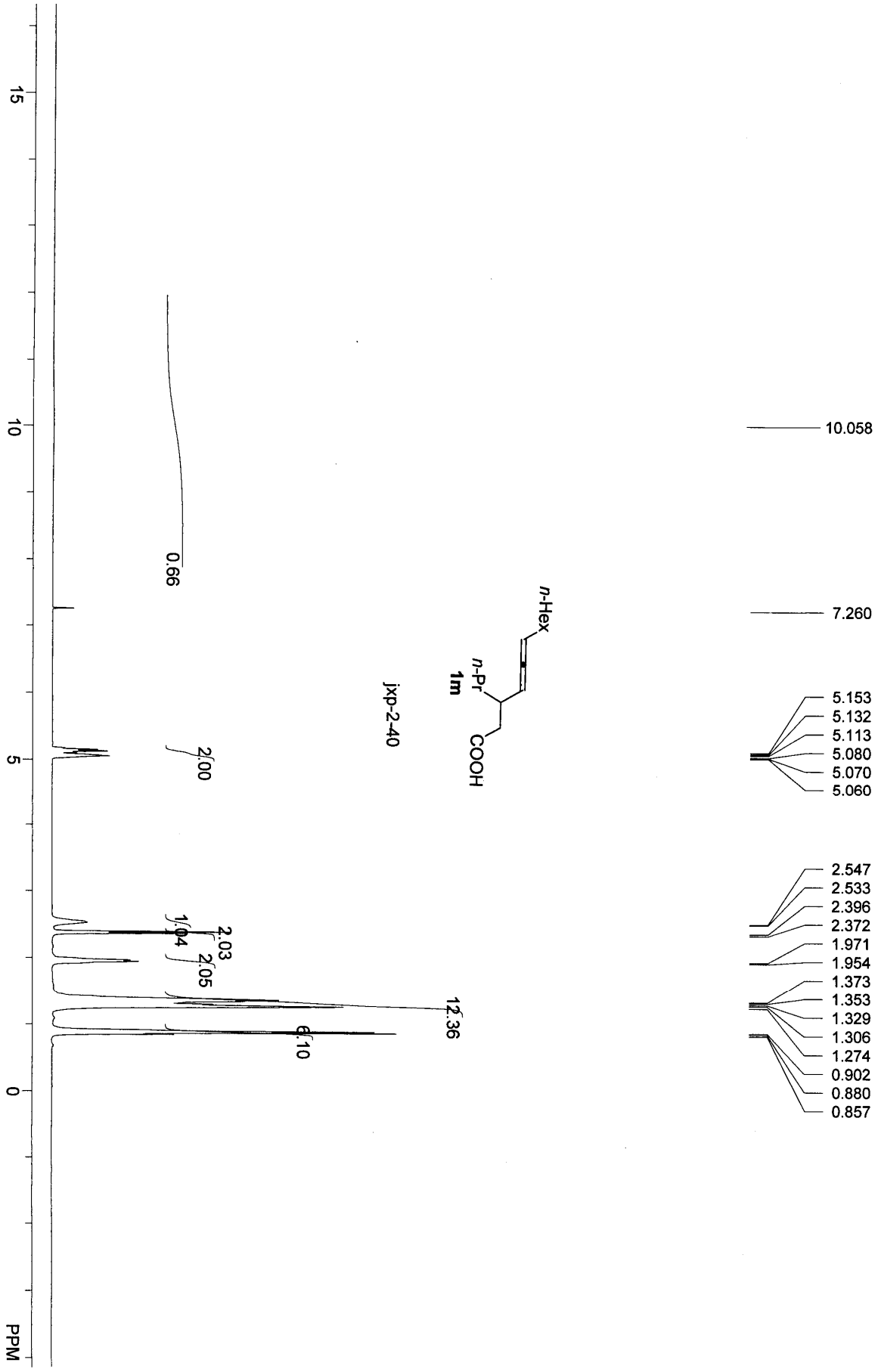
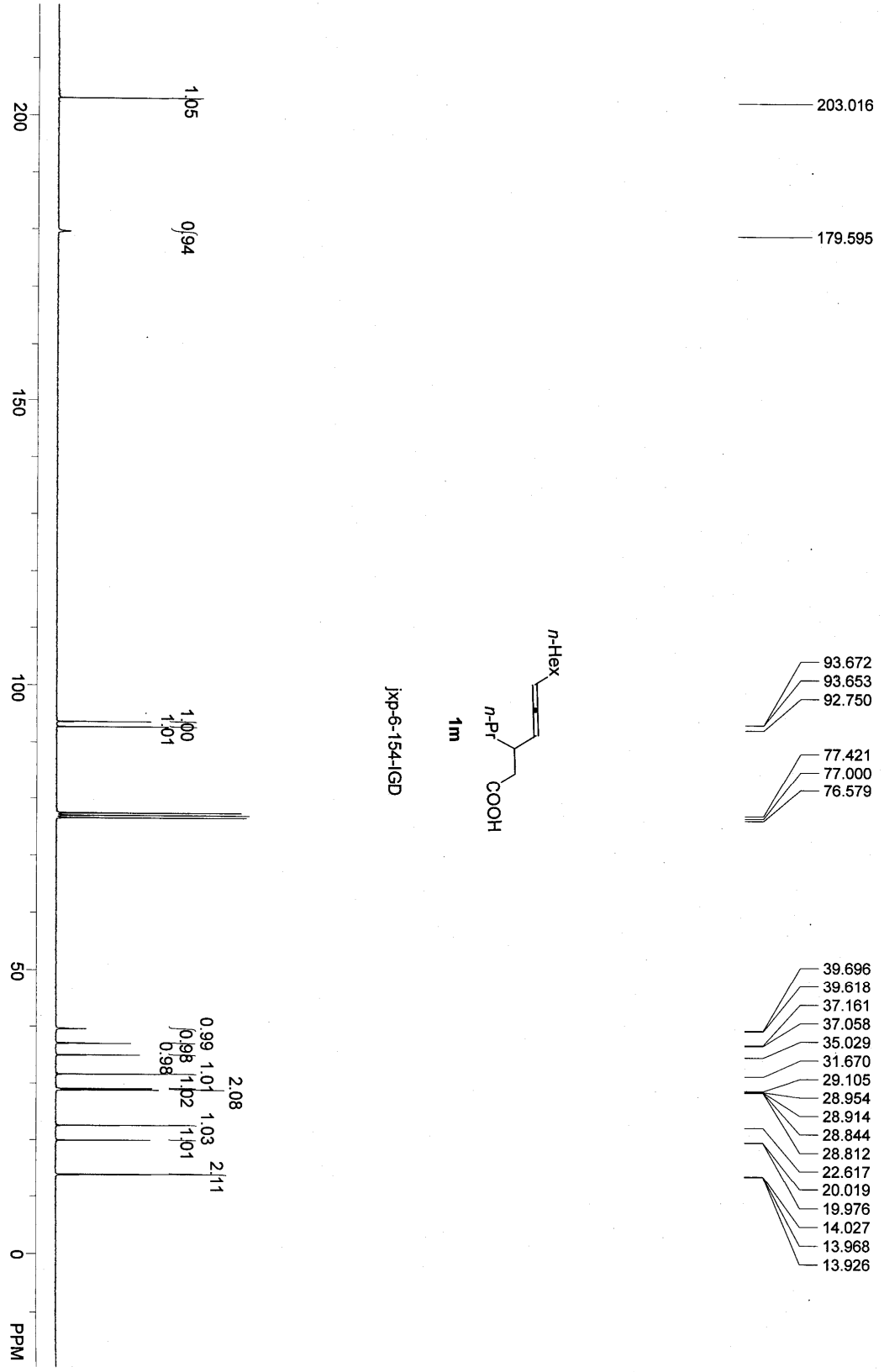
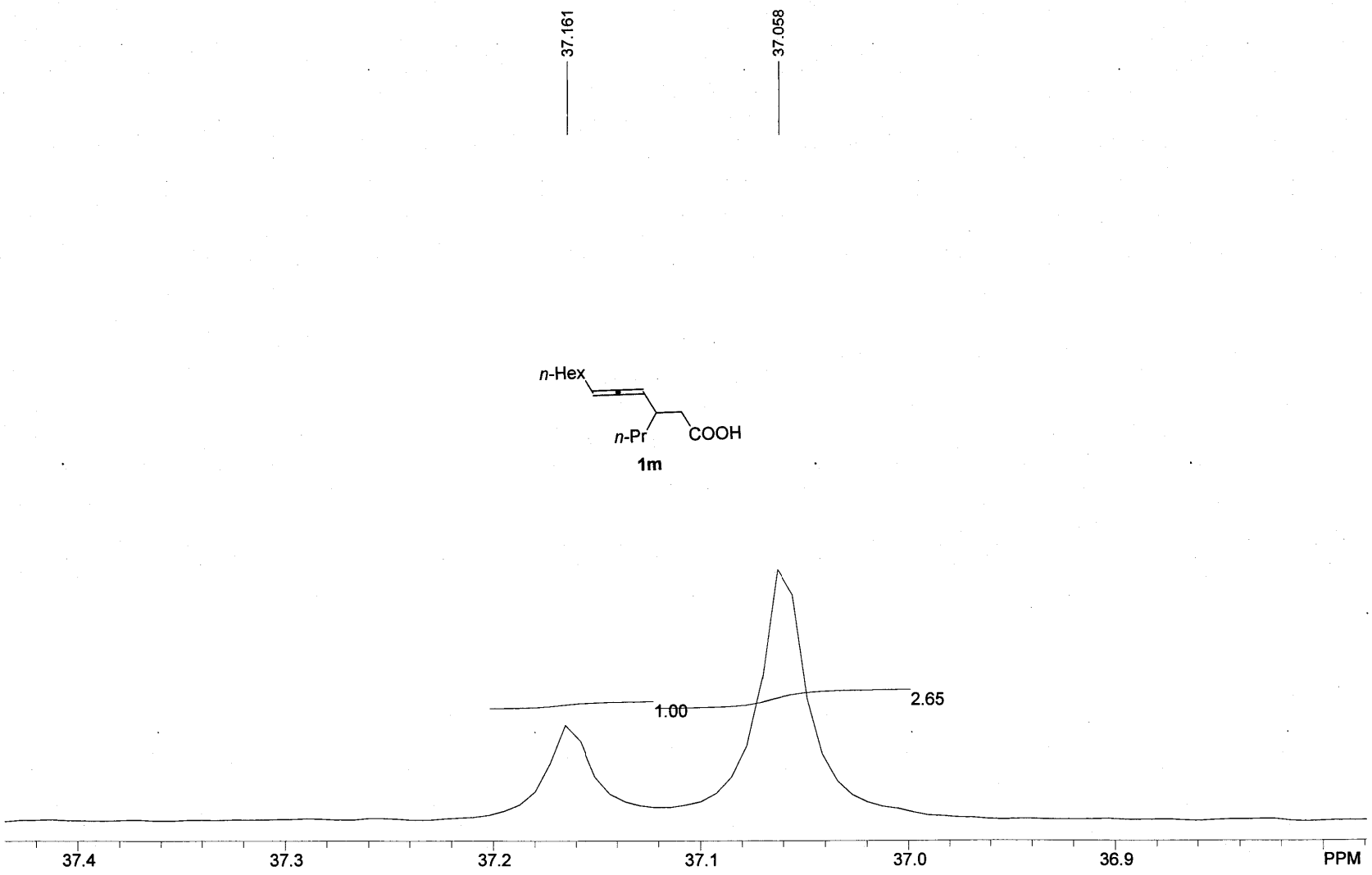
29.520
n-Bu
Me
COOH
1l
3.13
1.00
30.0
29.8
29.6
29.4
29.2
PPM


15
10
5
0
PPM
0.66
2.00
1.04
2.03
2.05
12.36
6.10
jxp-2-40
1m
n-Hex
n-Pr
COOH
10.058
7.260
5.153
5.132
5.113
5.080
5.070
5.060
2.547
2.533
2.396
2.372
1.971
1.954
1.373
1.353
1.329
1.306
1.274
0.902
0.880
0.857

Inverse gated decoupling ^{13}C NMR analysis for the determination of the *dr* value of **1m.**

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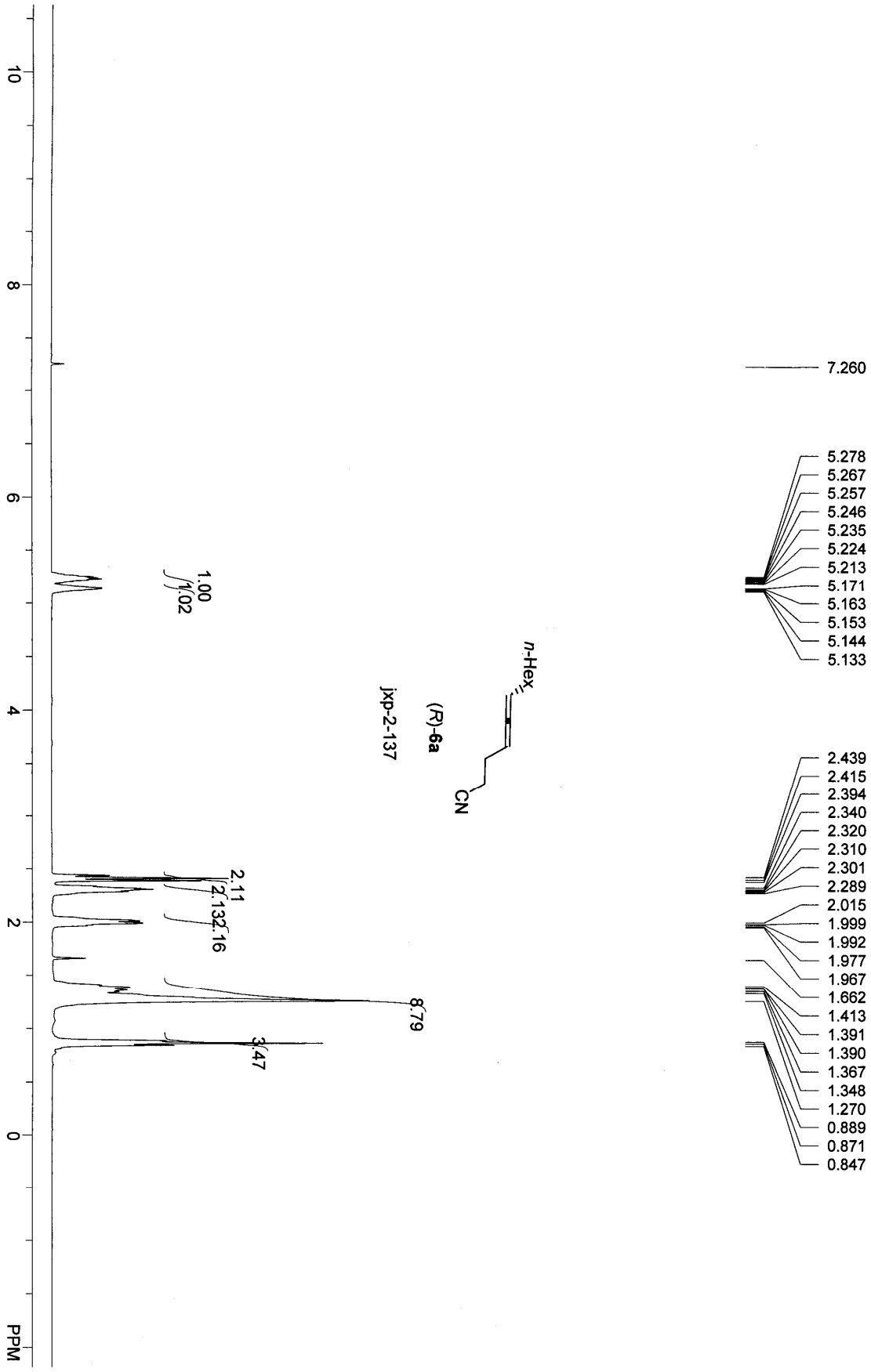
37.058
n-Hex
n-Pr
COOH
1m
1.00
2.65
37.4
37.3
37.2
37.1
37.0
36.9
PPM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5.278
5.267
5.257
5.246
5.235
5.224
5.213
5.171
5.163
5.153
5.144
5.133
2.439
2.415
2.394
2.340
2.320
2.310
2.301
2.289
2.015
1.999
1.992
1.977
1.967
1.662
1.413
1.391
1.390
1.367
1.348
1.270
0.889
0.871
0.847
n-Hex
CN
(R)-6a
jxp-2-137
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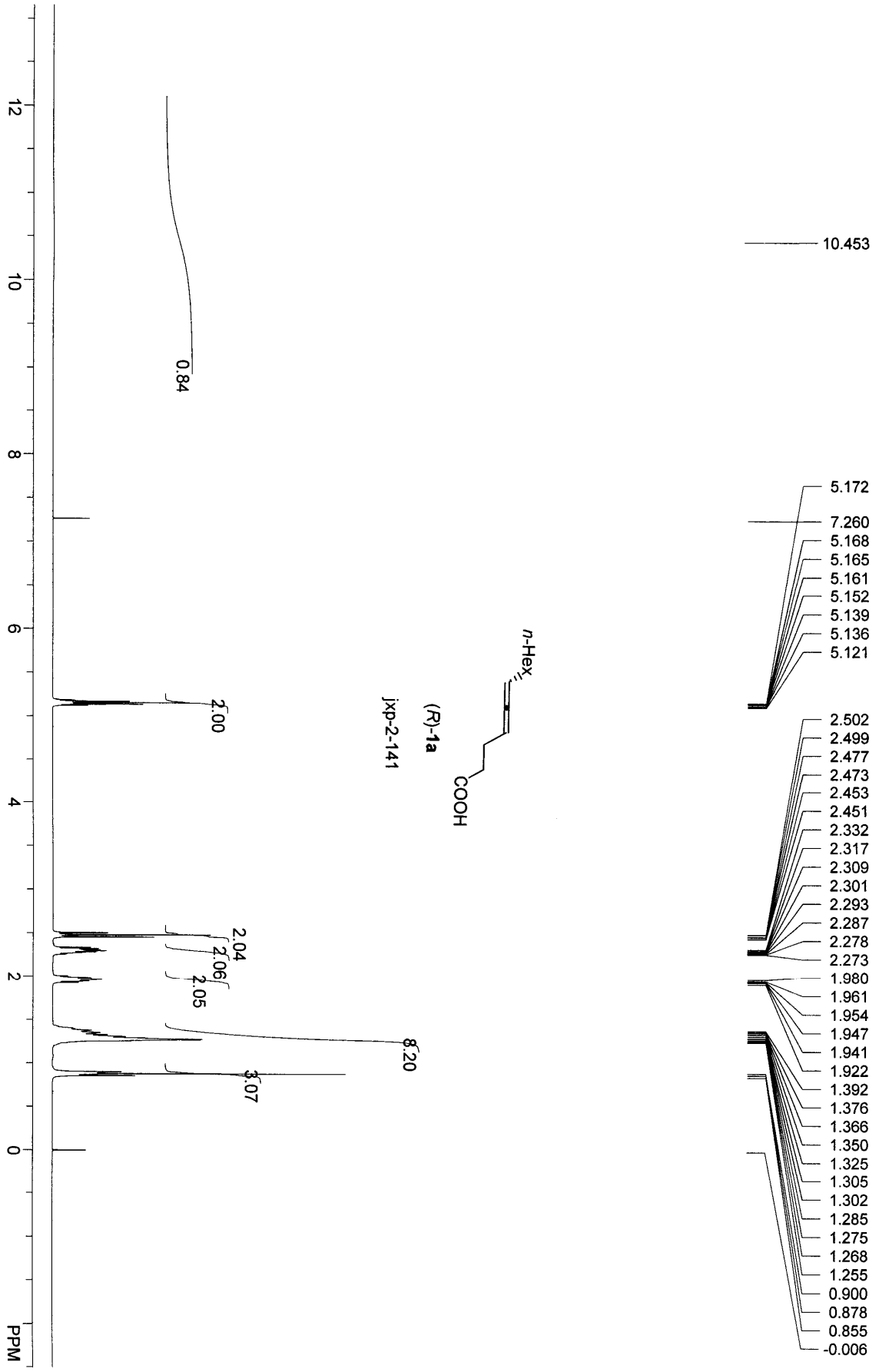
1.02
2.11
2.13
2.16
8.79
3.47
10
8
6
4
2
0
PPM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5.168
5.165
5.161
5.152
5.139
5.136
5.121
2.502
2.499
2.477
2.473
2.453
2.451
2.332
2.317
2.309
2.301
2.293
2.287
2.278
2.273
1.980
1.961
1.954
1.947
1.941
1.922
1.392
1.376
1.366
1.350
1.325
1.305
1.302
1.285
1.275
1.268
1.255
0.900
0.878
0.855
-0.006
n-Hex
COOH
(R)-1a
jxp-2-141
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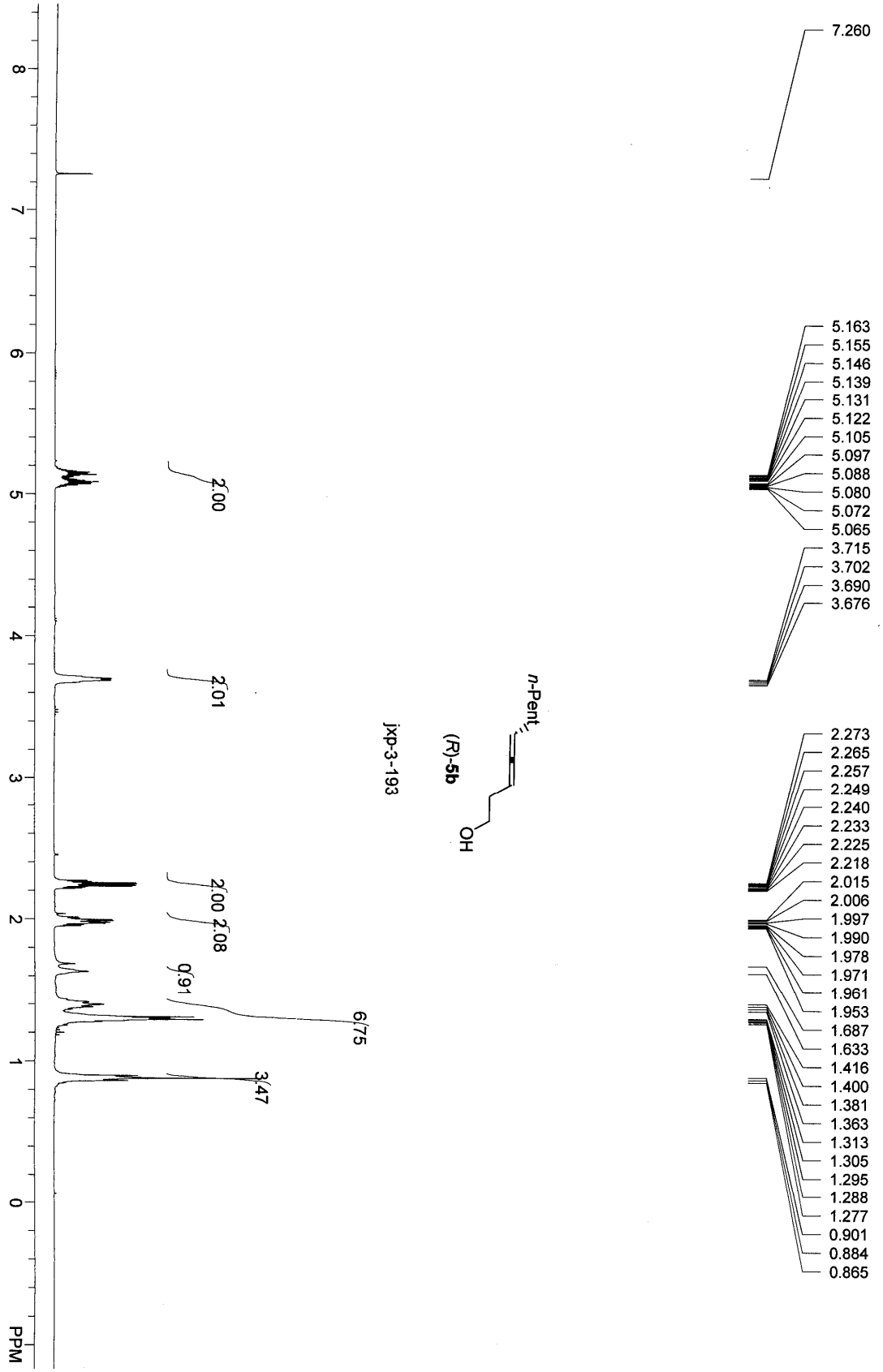
2.04
2.06
2.05
8.20
3.07
12
10
8
6
4
2
0
PPM


7.260
5.163
5.155
5.146
5.139
5.131
5.122
5.105
5.097
5.088
5.080
5.072
5.065
3.715
3.702
3.690
3.676
2.273
2.265
2.257
2.249
2.240
2.233
2.225
2.218
2.015
2.006
1.997
1.990
1.978
1.971
1.961
1.953
1.687
1.633
1.416
1.400
1.381
1.363
1.313
1.305
1.295
1.288
1.277
0.901
0.884
0.865
n-Pent
(R)-5b
OH
jxp-3-193
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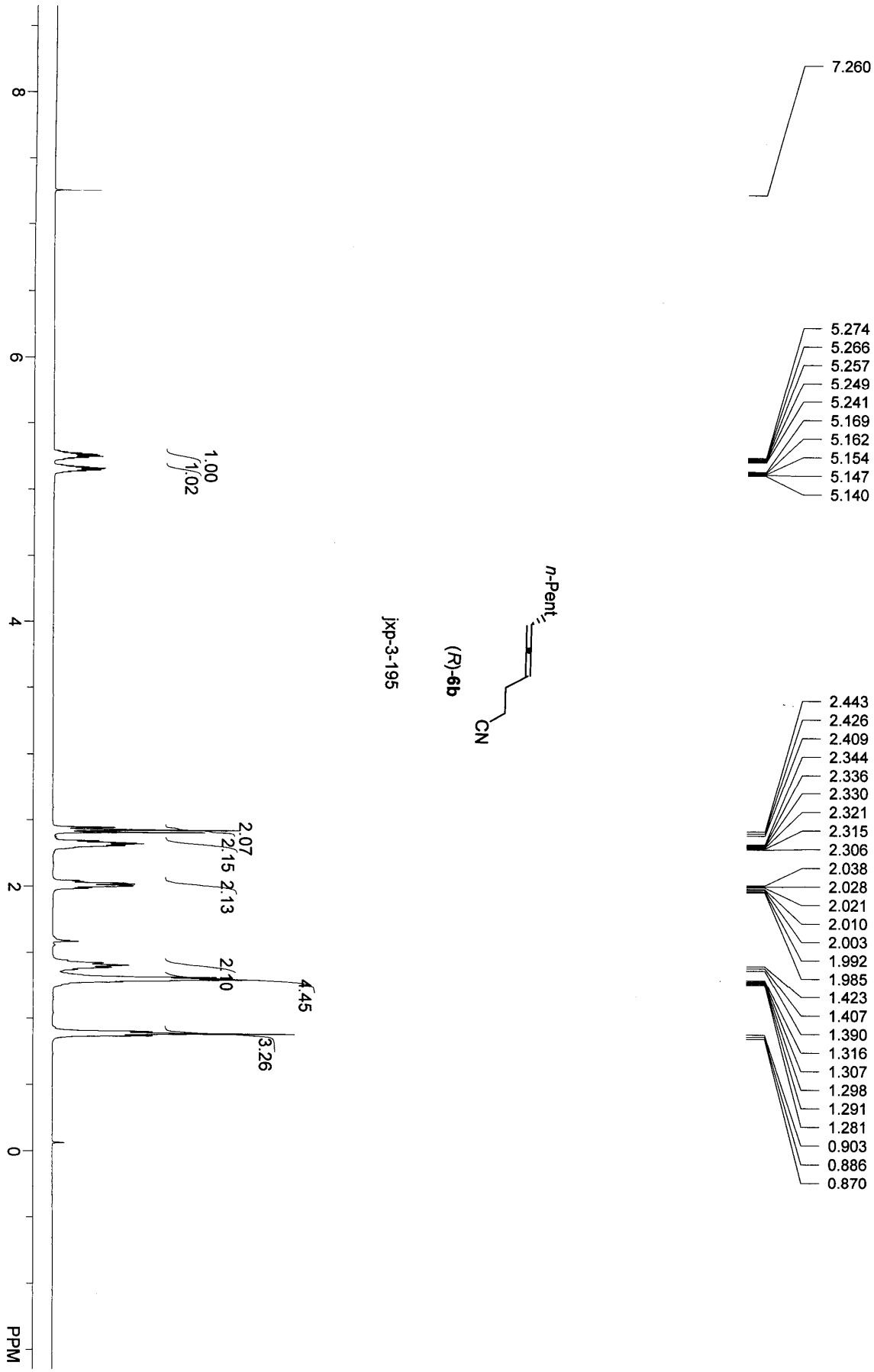
2.01
2.00
2.08
0.91
6.75
3.47
PPM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5.274
5.266
5.257
5.249
5.241
5.169
5.162
5.154
5.147
5.140
n-Pent
(R)-6b
CN
jxp-3-195
2.443
2.426
2.409
2.344
2.336
2.330
2.321
2.315
2.306
2.038
2.028
2.021
2.010
2.003
1.992
1.985
1.423
1.407
1.390
1.316
1.307
1.298
1.291
1.281
0.903
0.886
0.870
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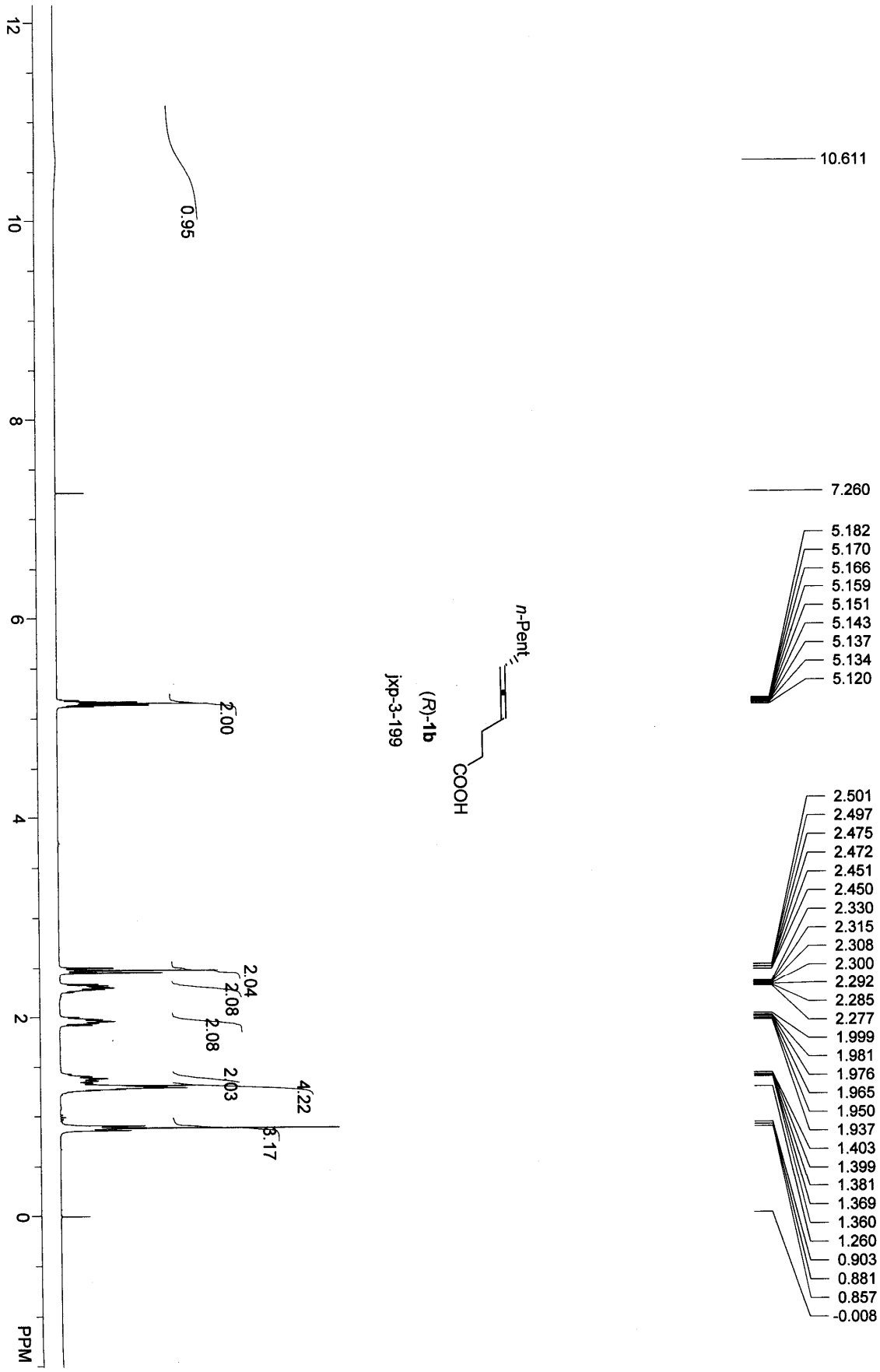
2.07
2.15
2.13
2.10
4.45
3.26
8
6
4
2
0
PPM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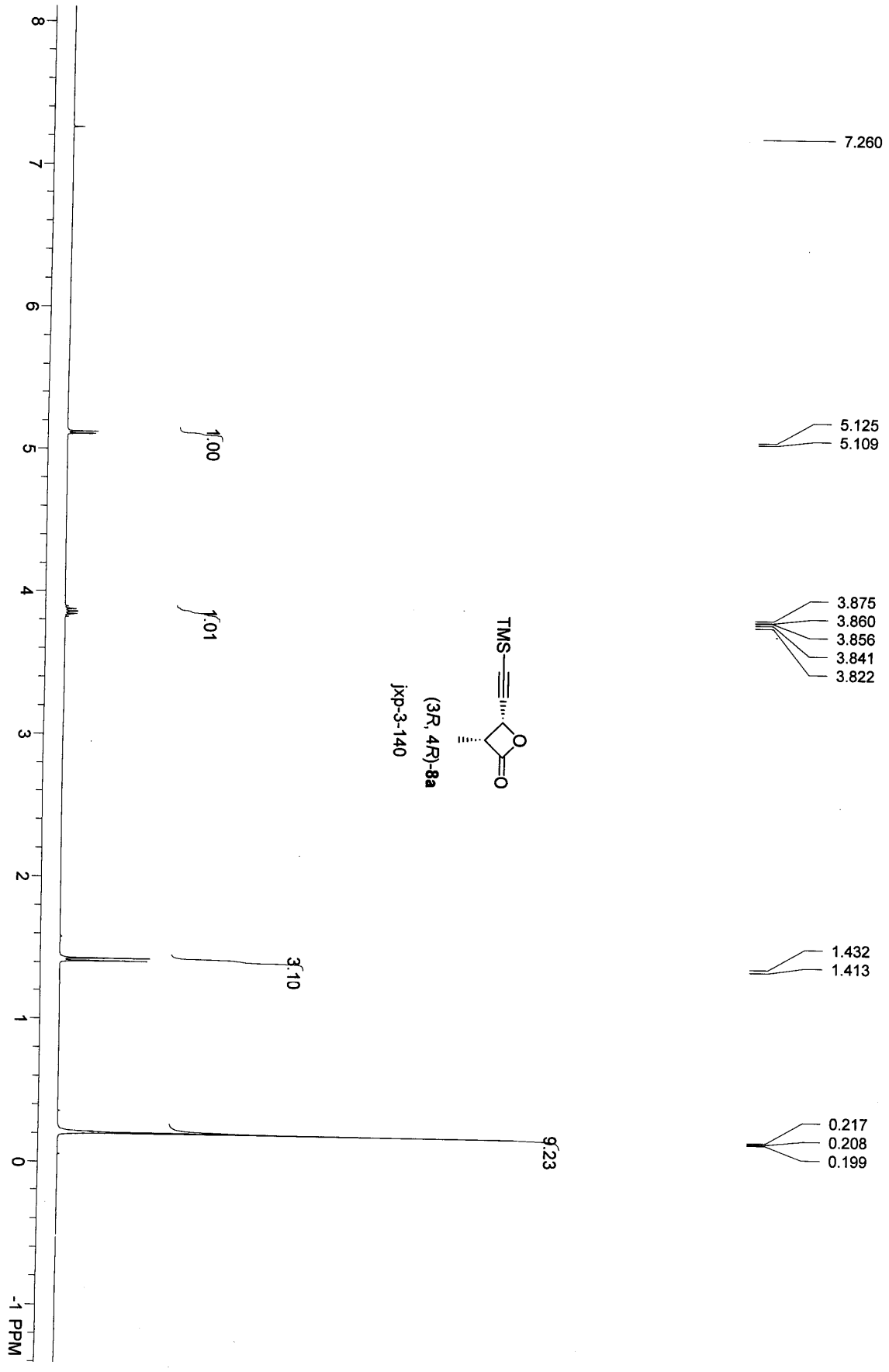
5.182
5.170
5.166
5.159
5.151
5.143
5.137
5.134
5.120
2.501
2.497
2.475
2.472
2.451
2.450
2.330
2.315
2.308
2.300
2.292
2.285
2.277
1.999
1.981
1.976
1.965
1.950
1.937
1.403
1.399
1.381
1.369
1.360
1.260
0.903
0.881
0.857
-0.008
n-Pent
COOH
(R)-1b
jxp-3-199
0.95
2.00
2.04
2.08
2.08
2.03
4.22
3.17
12
10
8
6
4
2
0
PPM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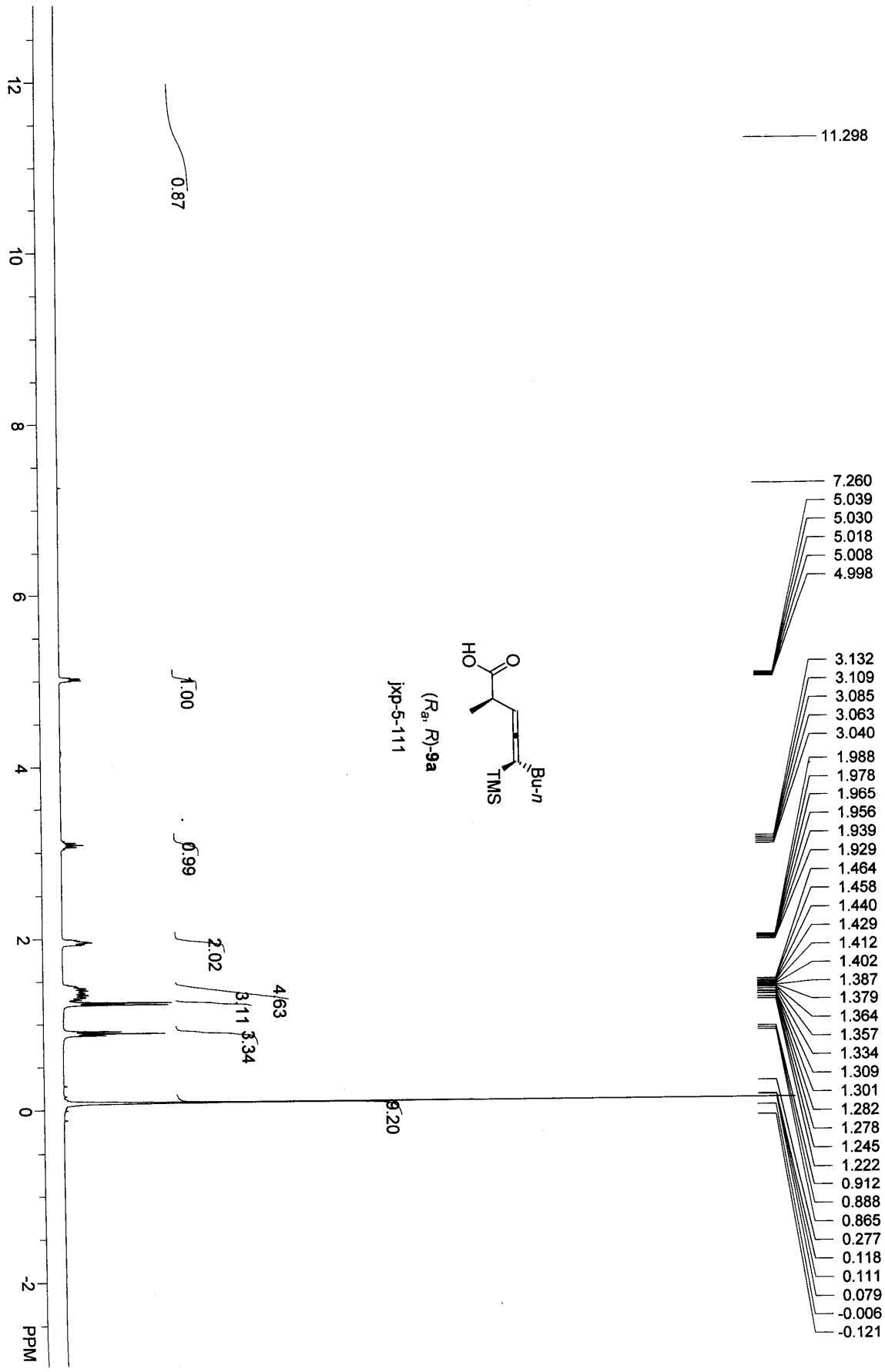
5.125
5.109
3.875
3.860
3.856
3.841
3.822
1.432
1.413
0.217
0.208
0.199
TMS
(3R, 4R)-8a
jxp-3-140
1.00
1.01
3.10
9.23
8
7
6
5
4
3
2
1
0
-1 PPM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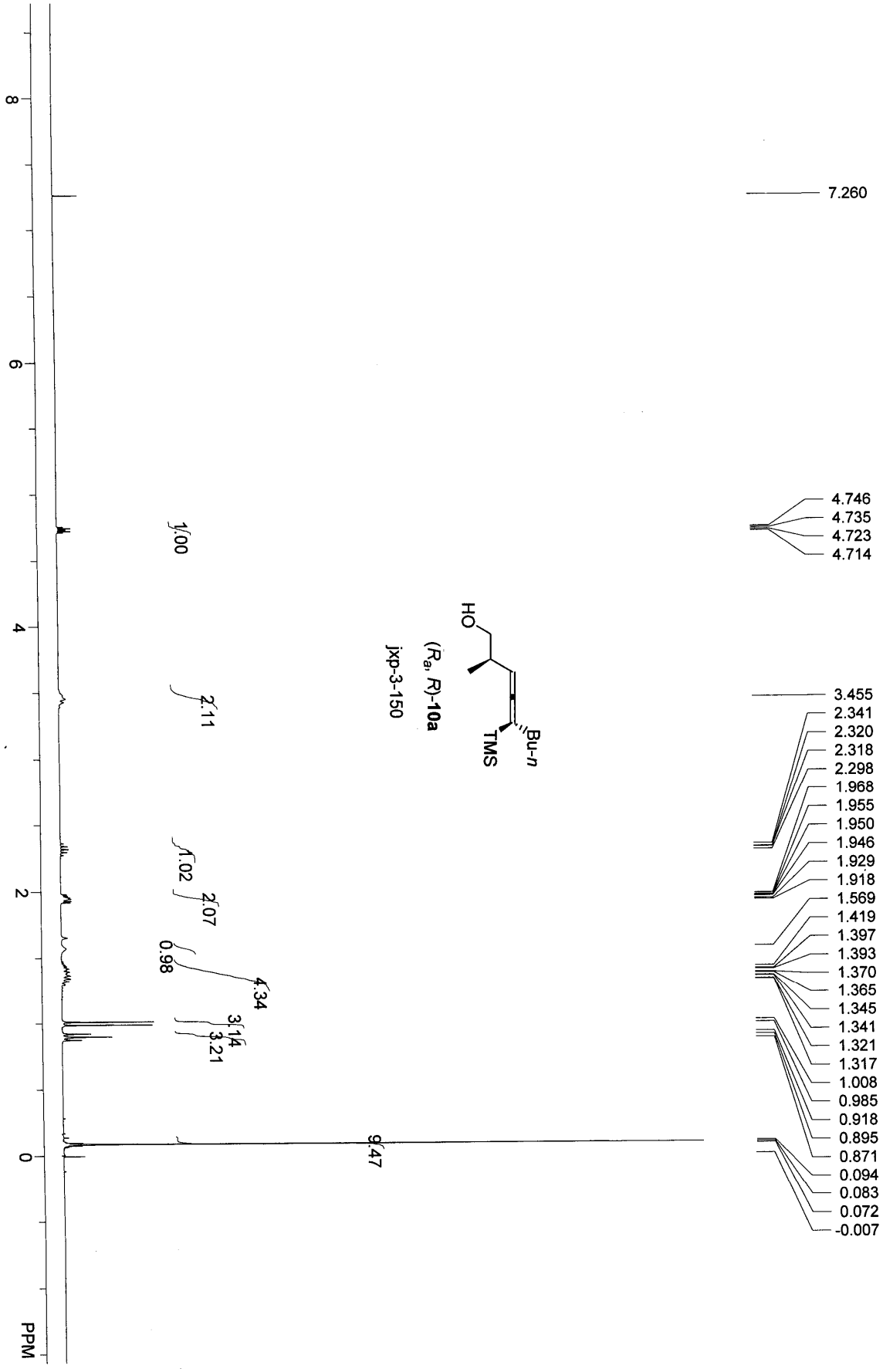
7.260
5.039
5.030
5.018
5.008
4.998
3.132
3.109
3.085
3.063
3.040
1.988
1.978
1.965
1.956
1.939
1.929
1.464
1.458
1.440
1.429
1.412
1.402
1.387
1.379
1.364
1.357
1.334
1.309
1.301
1.282
1.278
1.245
1.222
0.912
0.888
0.865
0.277
0.118
0.111
0.079
-0.006
-0.121
0.87
1.00
0.99
2.02
4.63
3.11
3.34
9.20
HO
O
TMS
Bu-n
(Ra, R)-9a
jxp-5-111
12
10
8
6
4
2
0
-2
PPM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4.735
4.723
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2.320
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2.298
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1.950
1.946
1.929
1.918
1.569
1.419
1.397
1.393
1.370
1.365
1.345
1.341
1.321
1.317
1.008
0.985
0.918
0.895
0.871
0.094
0.083
0.072
-0.007
HO
TMS
Bu-n
(Ra, R)-10a
jxp-3-150
1.00
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3.21
9.47
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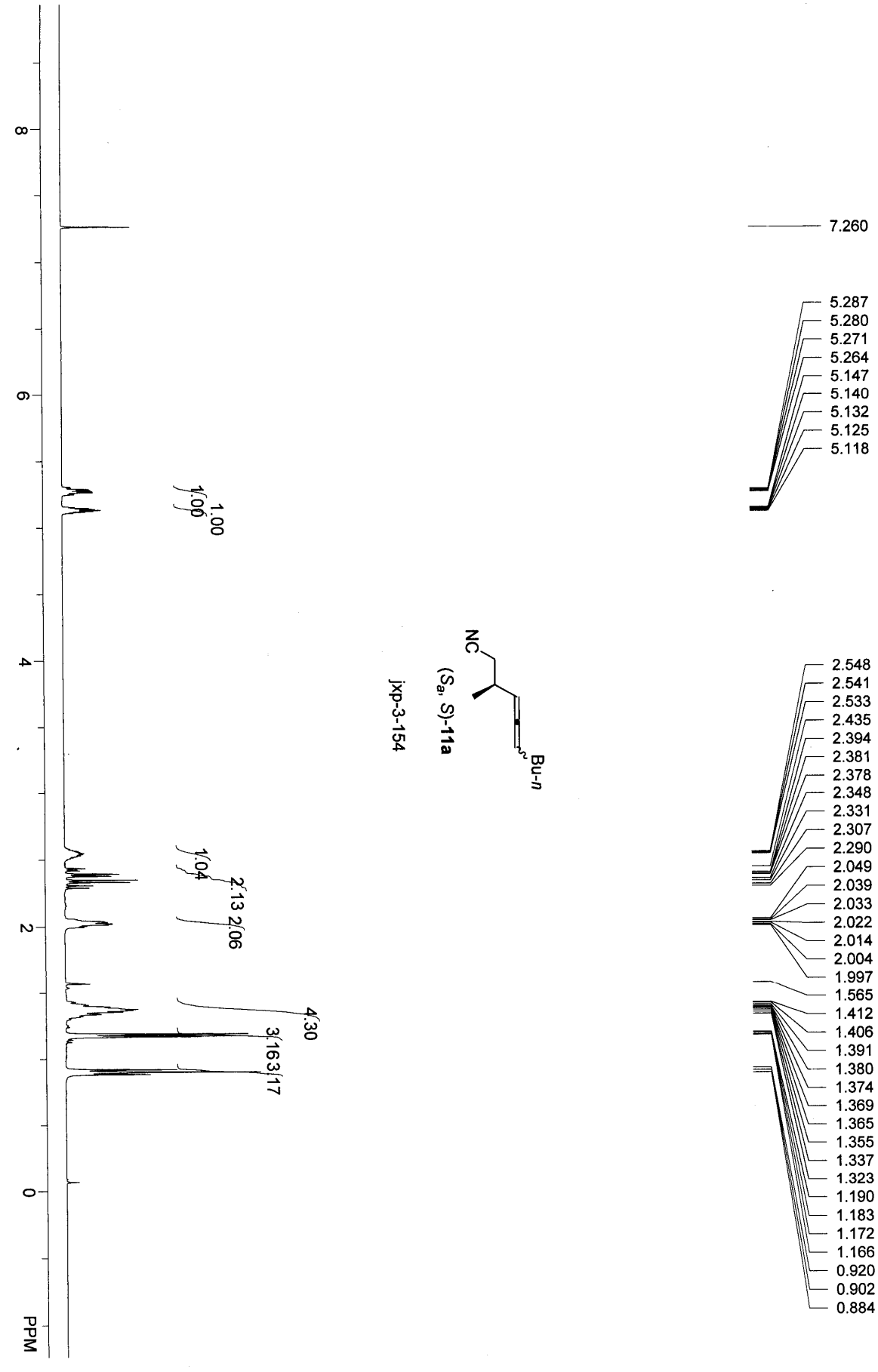
6
4
2
0
PPM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5.280
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5.264
5.147
5.140
5.132
5.125
5.118
2.548
2.541
2.533
2.435
2.394
2.381
2.378
2.348
2.331
2.307
2.290
2.049
2.039
2.033
2.022
2.014
2.004
1.997
1.565
1.412
1.406
1.391
1.380
1.374
1.369
1.365
1.355
1.337
1.323
1.190
1.183
1.172
1.166
0.920
0.902
0.884
NC
(Sa, S)-11a
Bu-n
jxp-3-154
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3.17
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4
2
0
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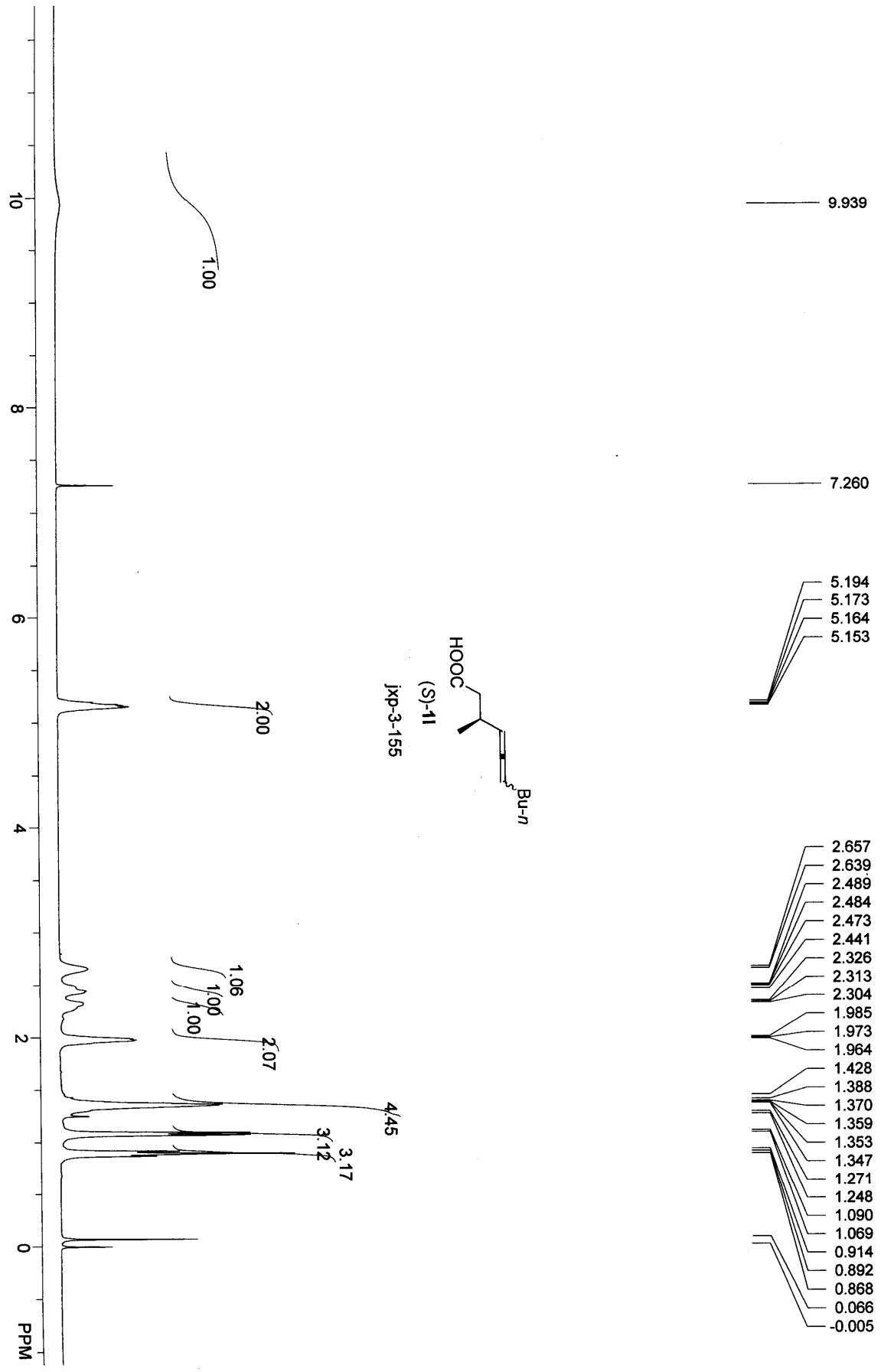
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5.173
5.164
5.153
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2.639
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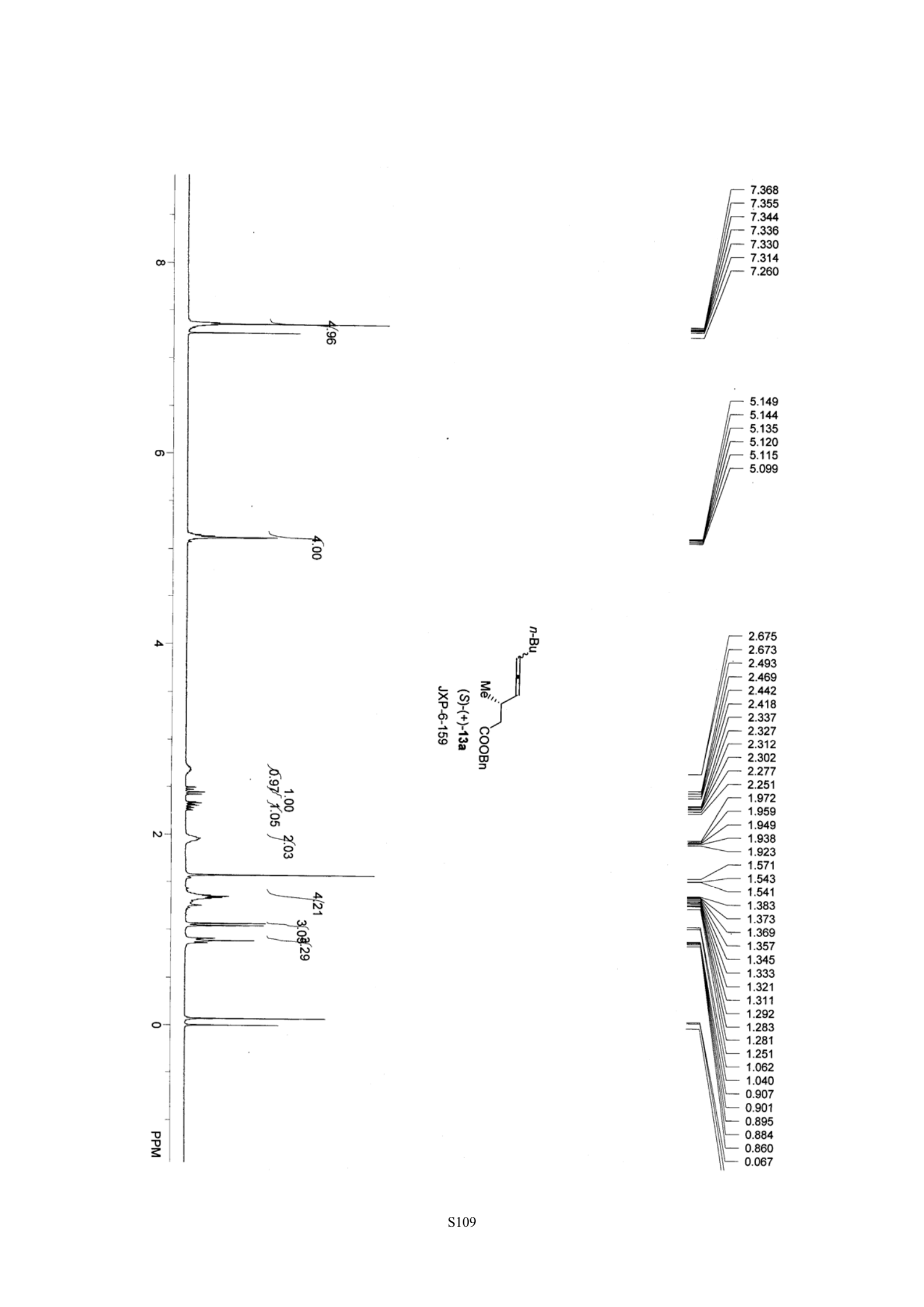
2.484
2.473
2.441
2.326
2.313
2.304
1.985
1.973
1.964
1.428
1.388
1.370
1.359
1.353
1.347
1.271
1.248
1.090
1.069
0.914
0.892
0.868
0.066
-0.005
HOOC
(S)-1l
jxp-3-155
Bu-n
1.00
2.00
1.06
1.00
1.00
2.07
4.45
3.12
3.17
10
8
6
4
2
0
PPM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7.344
7.336
7.330
7.314
7.260
5.149
5.144
5.135
5.120
5.115
5.099
2.675
2.673
2.493
2.469
2.442
2.418
2.337
2.327
2.312
2.302
2.277
2.251
1.972
1.959
1.949
1.938
1.923
1.571
1.543
1.541
1.383
1.373
1.369
1.357
1.345
1.333
1.321
1.311
1.292
1.283
1.281
1.251
1.062
1.040
0.907
0.901
0.895
0.884
0.860
0.067
n-Bu
Me
COOBn
(S)-(+)-13a
JXP-6-159
4.96
4.00
1.00
0.97
1.05
2.03
4.21
3.09
3.29
8
6
4
2
0
PPM

The HPLC spectrum of (*S*)-(+)-**13a**

Data File D:\HPCHEM\1\DATA\JXP\JXP00248.D Sample Name: jxp-6-81-sx

n-hexane/i-propanol=100/0; 214nm; 0.5 ml/min; AS-H

```
==========================================================================
Injection Date  : 5/11/2008 1:05:56 PM
Sample Name     : jxp-6-81-sx                    Location :   -
Acq. Operator   : jxp
Method          : D:\HPCHEM\1\METHODS\ERIC.M
Last changed    : 5/11/2008 12:46:11 PM by jxp
                  (modified after loading)
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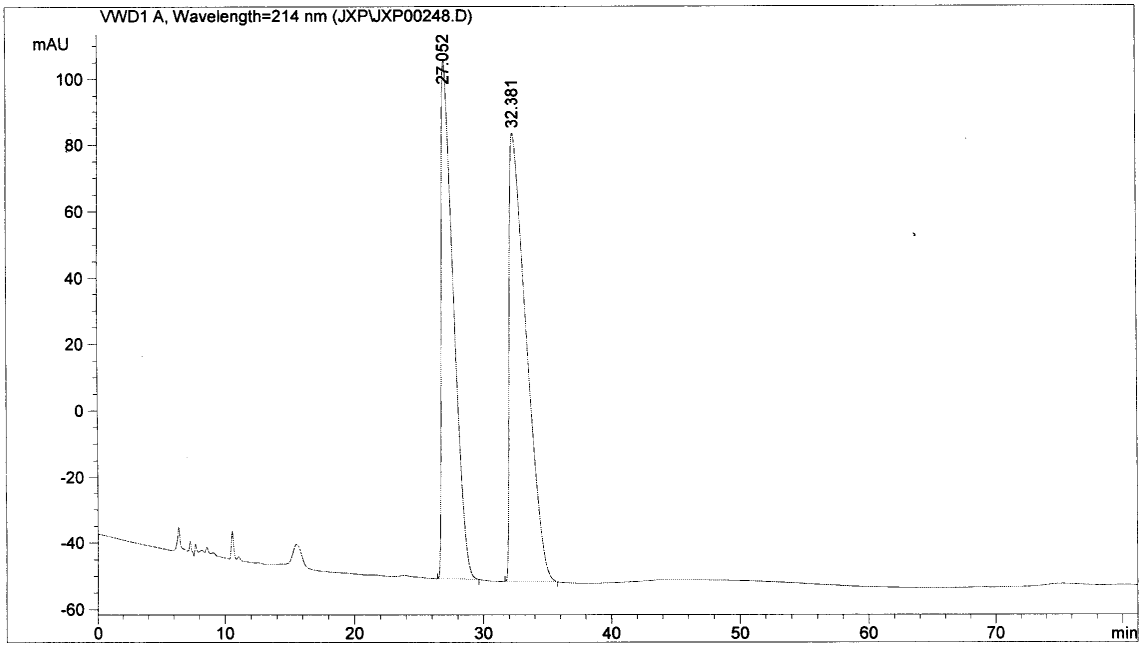


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==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=214 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  27.052 PB    0.9739 1.02002e4   156.30734  45.0796
   2  32.381 BB    1.3396 1.24268e4   135.09433  54.9204

Totals :                  2.26270e4   291.40167

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
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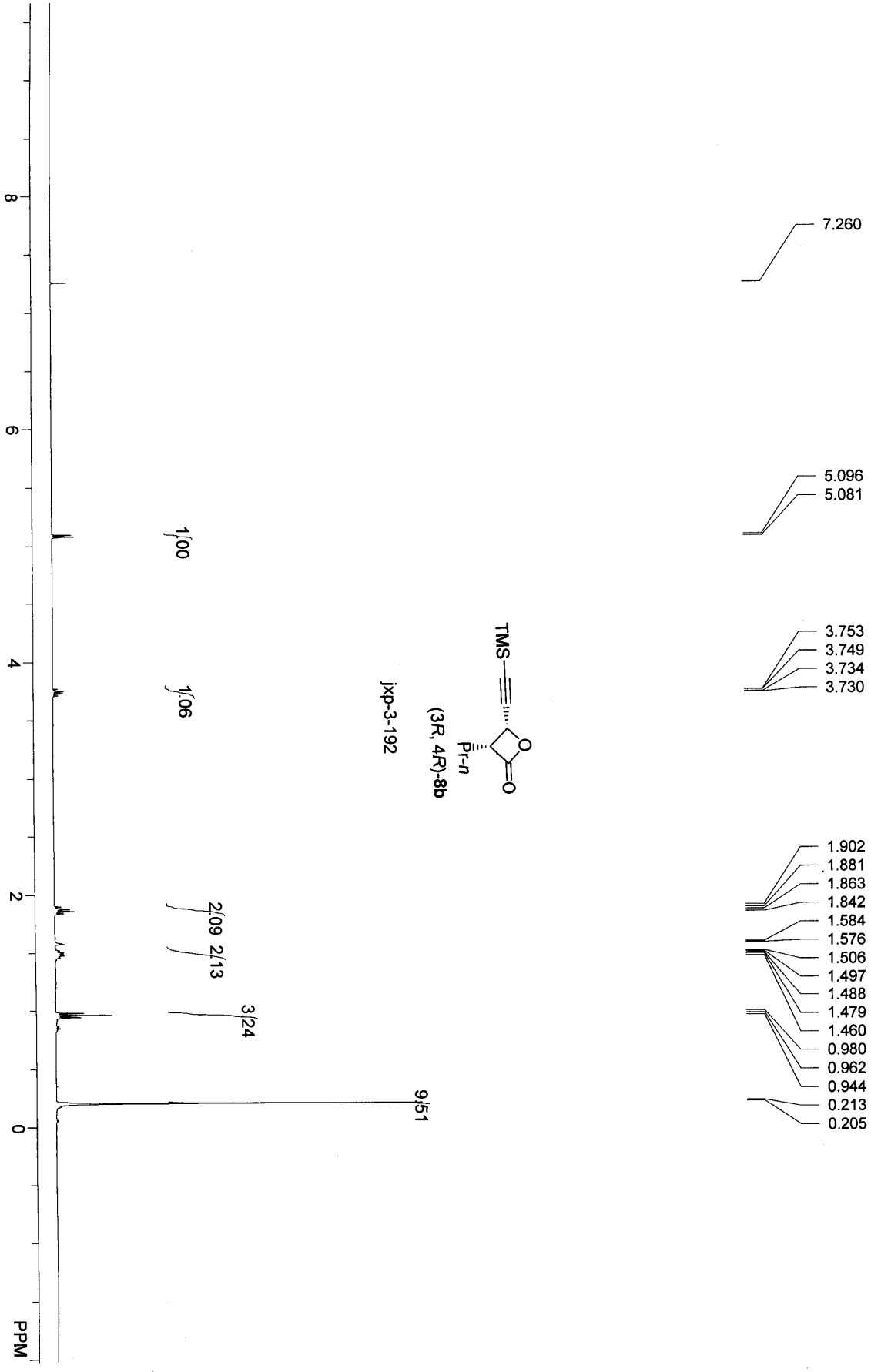
Instrument 1 5/11/2008 2:40:05 PM jxp Page 1 of 1


7.260
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5.081
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1.902
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1.842
1.584
1.576
1.506
1.497
1.488
1.479
1.460
0.980
0.962
0.944
0.213
0.205
TMS
n-Pr
O
O
(3R, 4R)-8b
jxp-3-192
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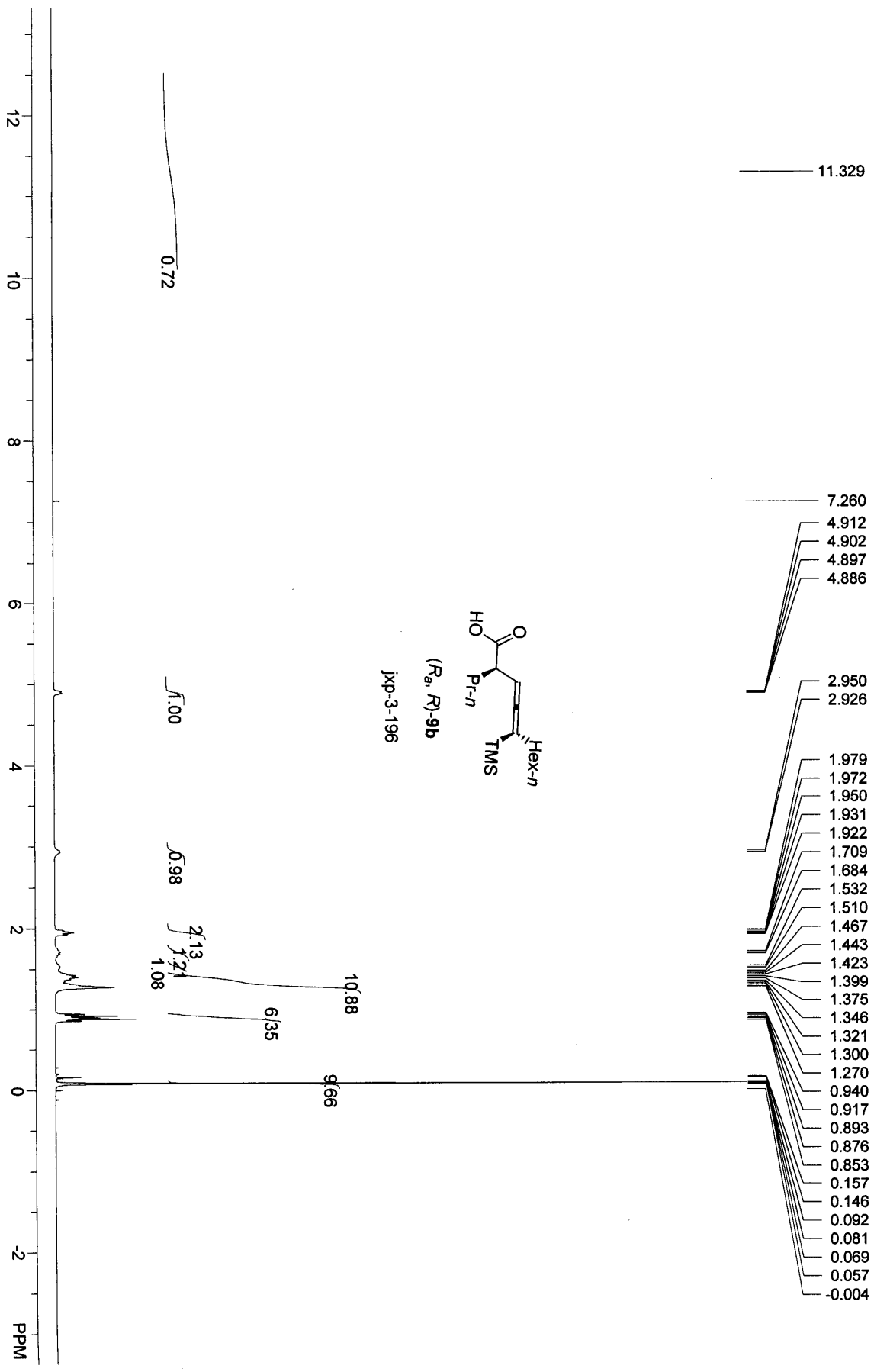
11.329
7.260
4.912
4.902
4.897
4.886
2.950
2.926
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1.972
1.950
1.931
1.922
1.709
1.684
1.532
1.510
1.467
1.443
1.423
1.399
1.375
1.346
1.321
1.300
1.270
0.940
0.917
0.893
0.876
0.853
0.157
0.146
0.092
0.081
0.069
0.057
-0.004
HO
O
Pr-n
TMS
Hex-n
(Ra, R)-9b
jxp-3-196
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1.00
0.98
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10
8
6
4
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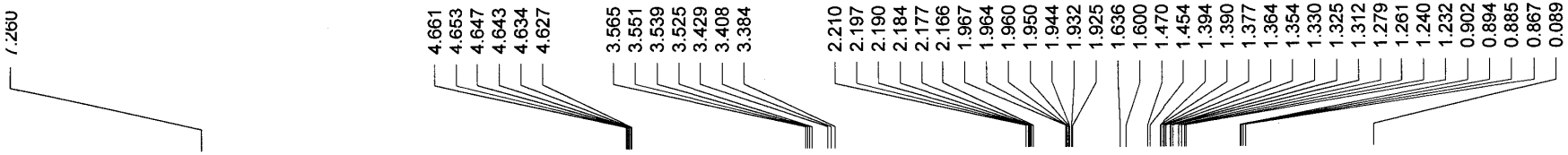
0
-2
PPM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3.539
3.525
3.429
3.408
3.384
2.210
2.197
2.190
2.184
2.177
2.166
1.967
1.964
1.960
1.950
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1.932
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1.600
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1.390
1.377
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1.354
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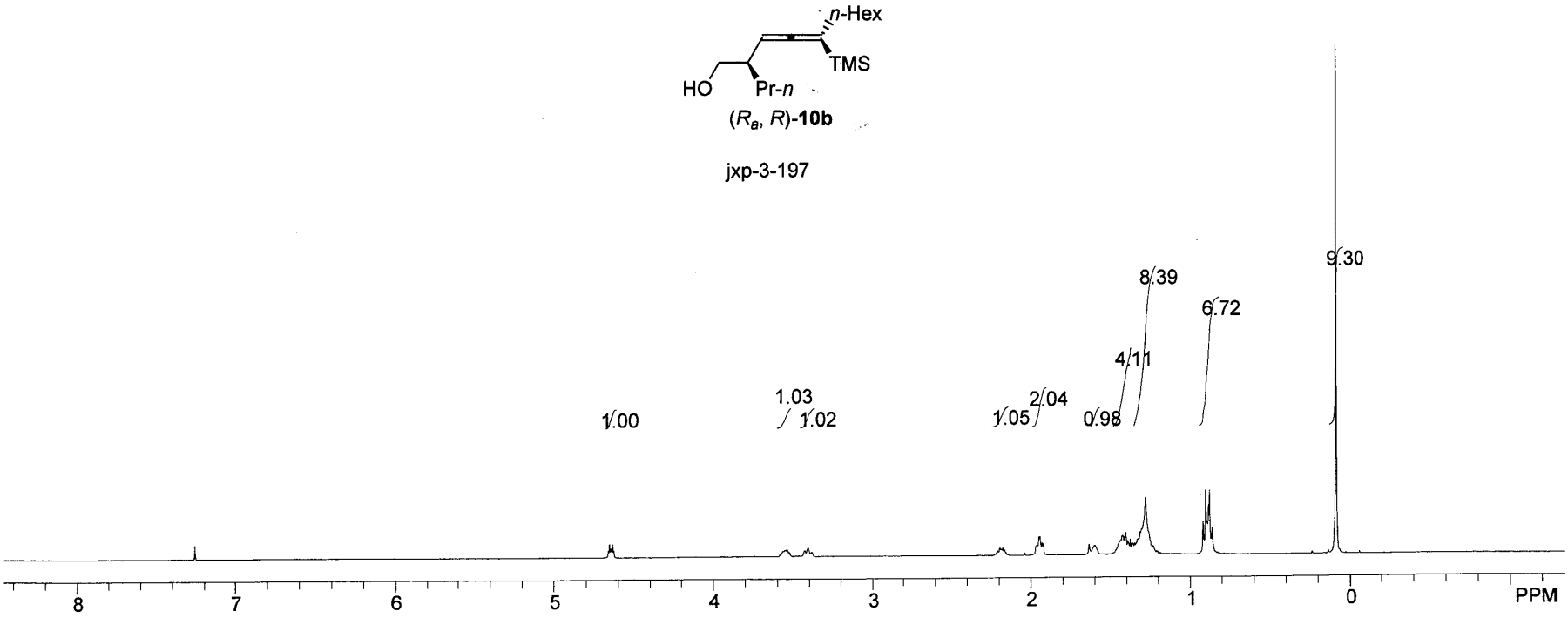
0.885
0.867
0.089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TMS
HO
Pr-n
(Ra, R)-10b
jxp-3-197
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1.02
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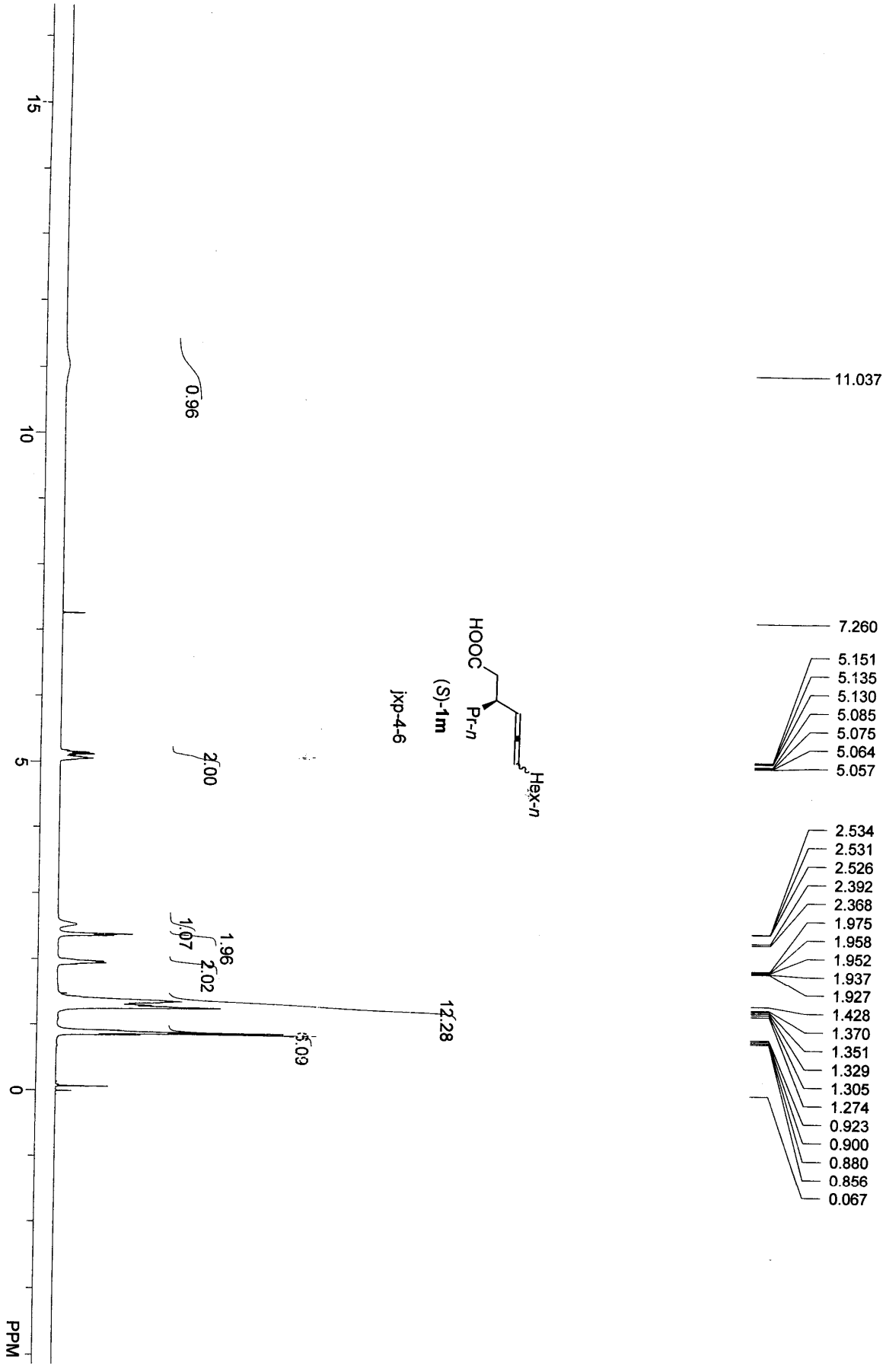
4.11
8.39
6.72
9.30
8
7
6
5
4
3
2
1
0
PPM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10
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1.96
1.07
2.02
12.28
5.09
HOOC
Pr-n
Hex-n
(S)-1m
jxp-4-6
11.037
7.260
5.151
5.135
5.130
5.085
5.075
5.064
5.057
2.534
2.531
2.526
2.392
2.368
1.975
1.958
1.952
1.937
1.927
1.428
1.370
1.351
1.329
1.305
1.274
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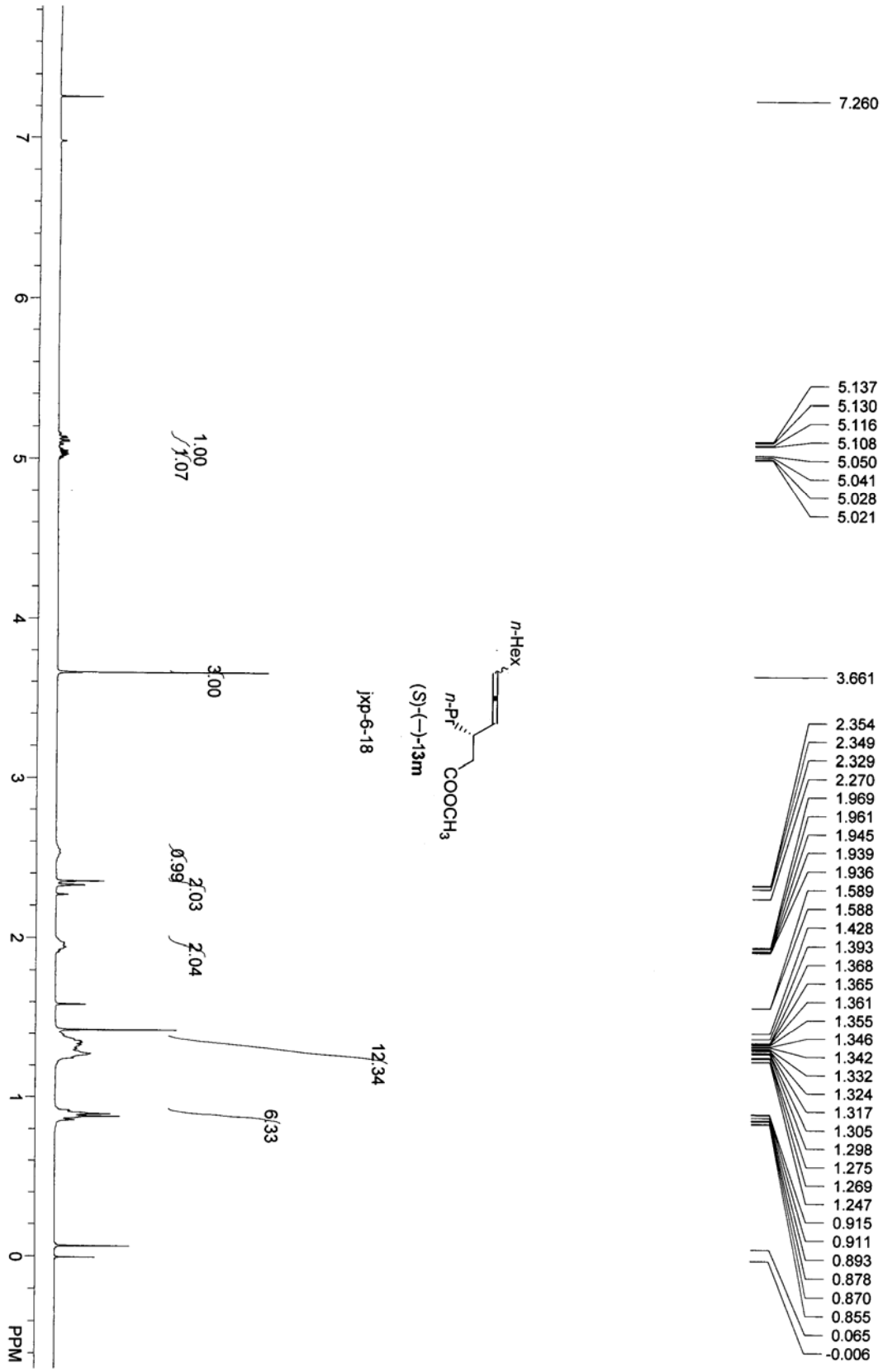
0.900
0.880
0.856
0.067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5.137
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5.108
5.050
5.041
5.028
5.021
3.661
2.354
2.349
2.329
2.270
1.969
1.961
1.945
1.939
1.936
1.589
1.588
1.428
1.393
1.368
1.365
1.361
1.355
1.346
1.342
1.332
1.324
1.317
1.305
1.298
1.275
1.269
1.247
0.915
0.911
0.893
0.878
0.870
0.855
0.065
-0.006
n-Hex
n-Pr
COOCH3
(S)-(−)-13m
jxp-6-18
1.00
1.07
3.00
0.99
2.03
2.04
12.34
6.33
PPM

The GC spectrum of (S)-(−)-**13m**

Data File C:\HPCHEM\1\DATA\SIG10333.D   Sample Name: jxp-6-18

```
=====================================================================
Injection Date  : 2008-3-28 8:35:00 下午
Sample Name     : jxp-6-18                    Location : Vial 1
Acq. Operator   : maff-6                           Inj :   1
                                            Inj Volume : External
Acq. Method     : C:\HPCHEM\1\METHODS\READY GC.M
Last changed    : 2008-3-28 8:22:25 下午 by maff-6
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\READY GC.M
Last changed    : 2008-3-28 9:16:11 下午 by maff-6
                  (modified after loading)
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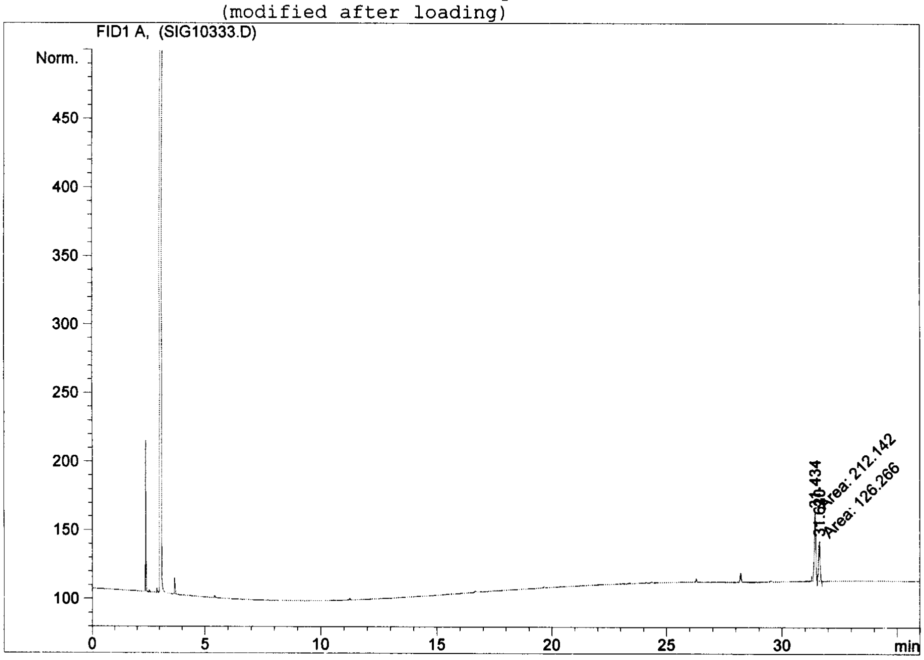


Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	31.434	MF	0.0705	212.14174	50.13708	62.68814
2	31.620	FM	0.0722	126.26637	29.14004	37.31186

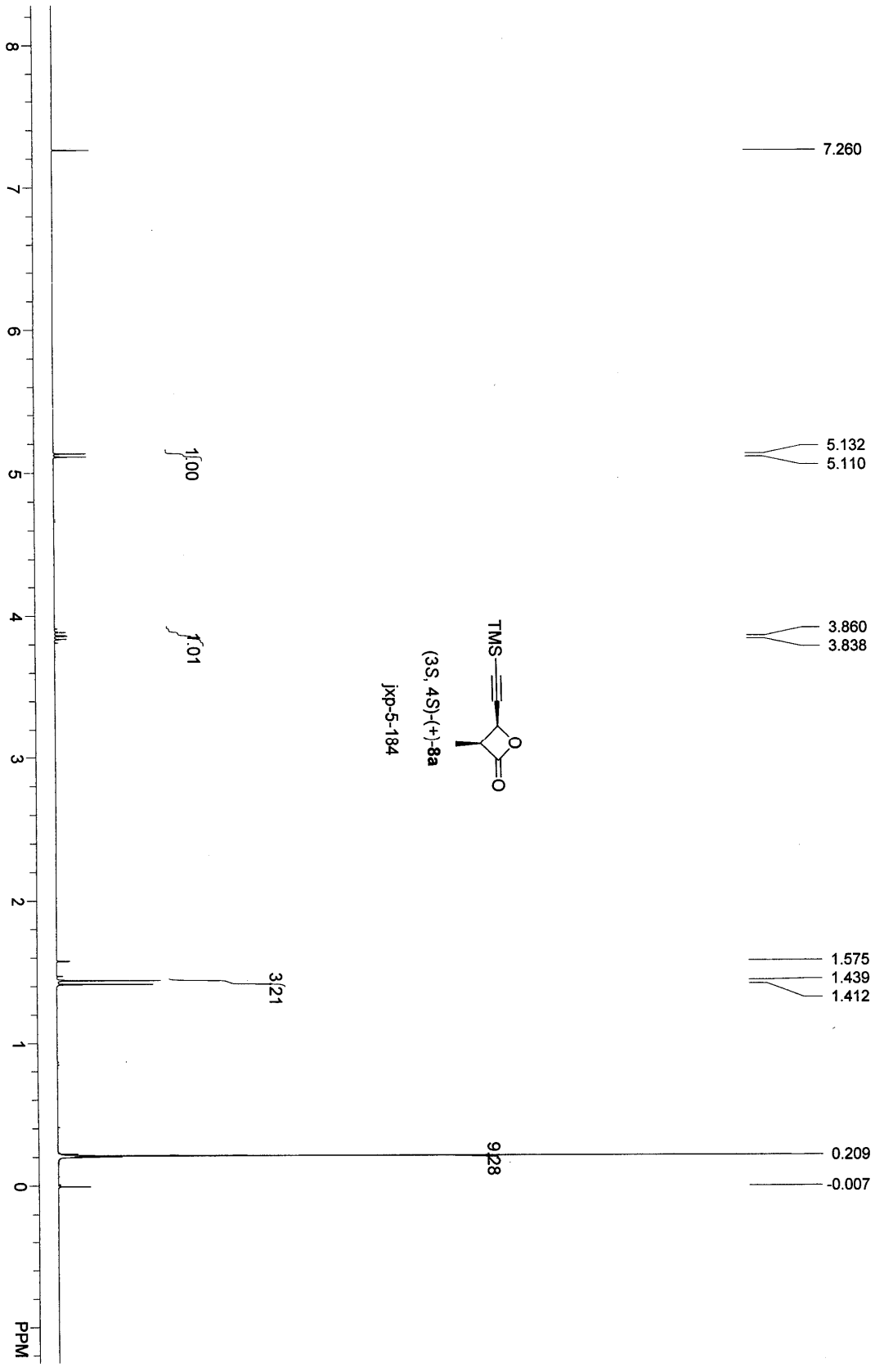
Totals : 338.40811 79.27711

HP-INNOWAX [illegible]
180 (1) 10.0 psi

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 2008-3-28 9:16:15 下午 maff-6   Page 1 of 1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5.132
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3.860
3.838
1.575
1.439
1.412
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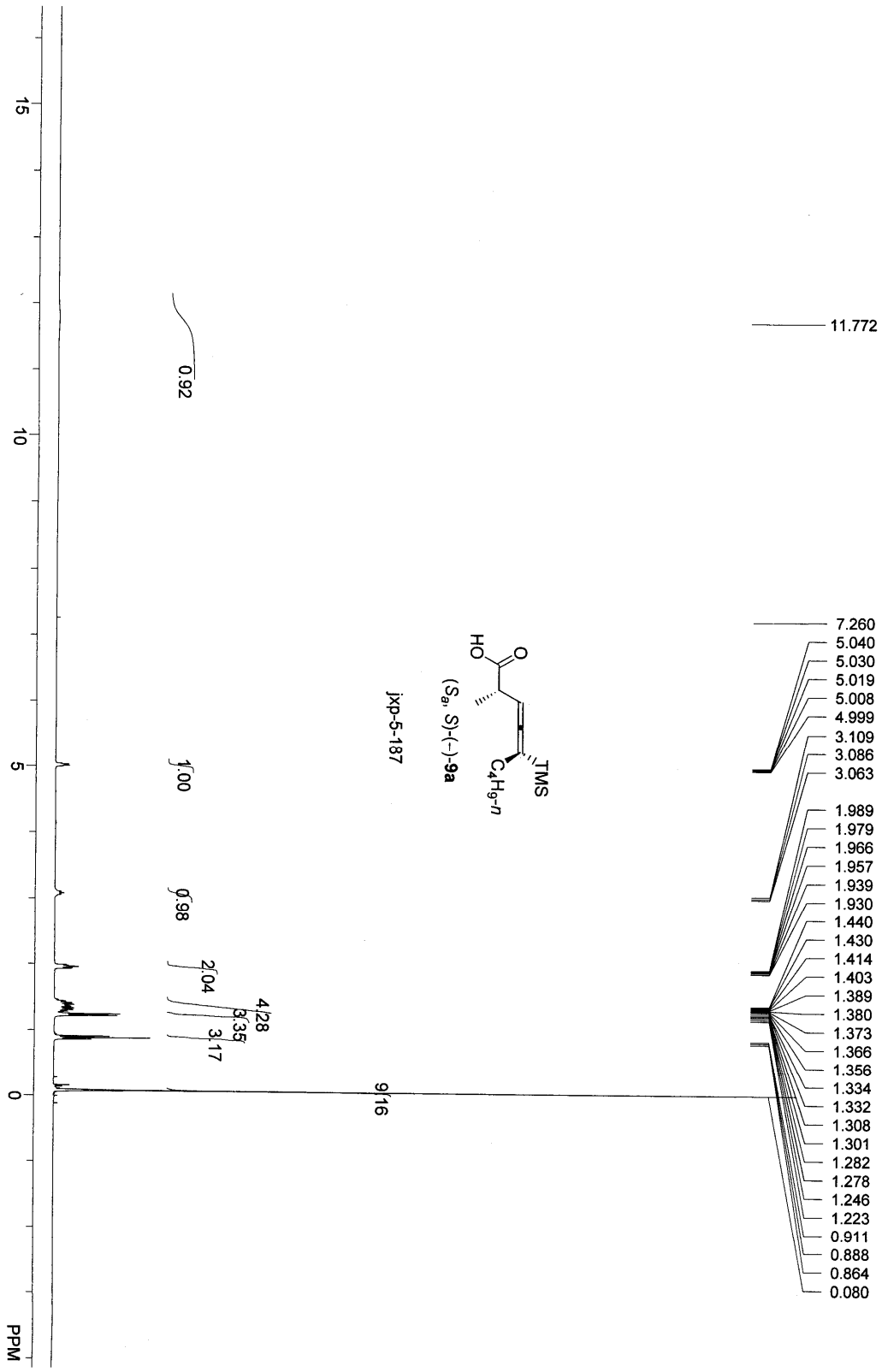
-0.007
1.00
1.01
3.21
9.28
TMS
O
O
(3S, 4S)-(+)-8a
jxp-5-184
PPM
8
7
6
5
4
3
2
1
0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5.040
5.030
5.019
5.008
4.999
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3.063
1.989
1.979
1.966
1.957
1.939
1.930
1.440
1.430
1.414
1.403
1.389
1.380
1.373
1.366
1.356
1.334
1.332
1.308
1.301
1.282
1.278
1.246
1.223
0.911
0.888
0.864
0.080
0.92
1.00
0.98
2.04
4.28
3.35
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9.16
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(Sa, S)-(-)-9a
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O
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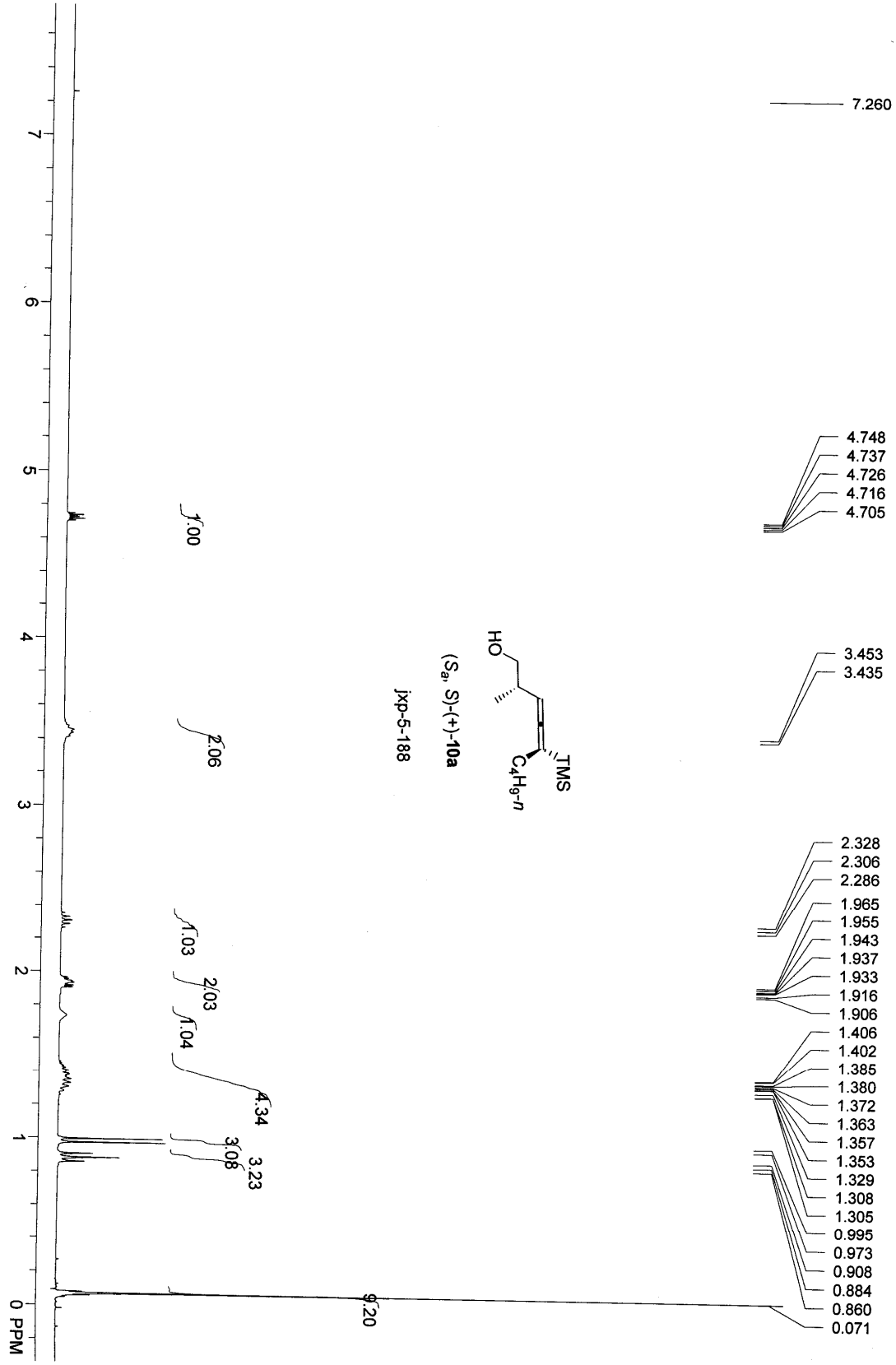
C4H9-n
15
10
5
0
PPM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4.716
4.705
3.453
3.435
2.328
2.306
2.286
1.965
1.955
1.943
1.937
1.933
1.916
1.906
1.406
1.402
1.385
1.380
1.372
1.363
1.357
1.353
1.329
1.308
1.305
0.995
0.973
0.908
0.884
0.860
0.071
HO
TMS
C4H9-n
(Sa, S)-(+)-10a
jxp-5-188
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2.06
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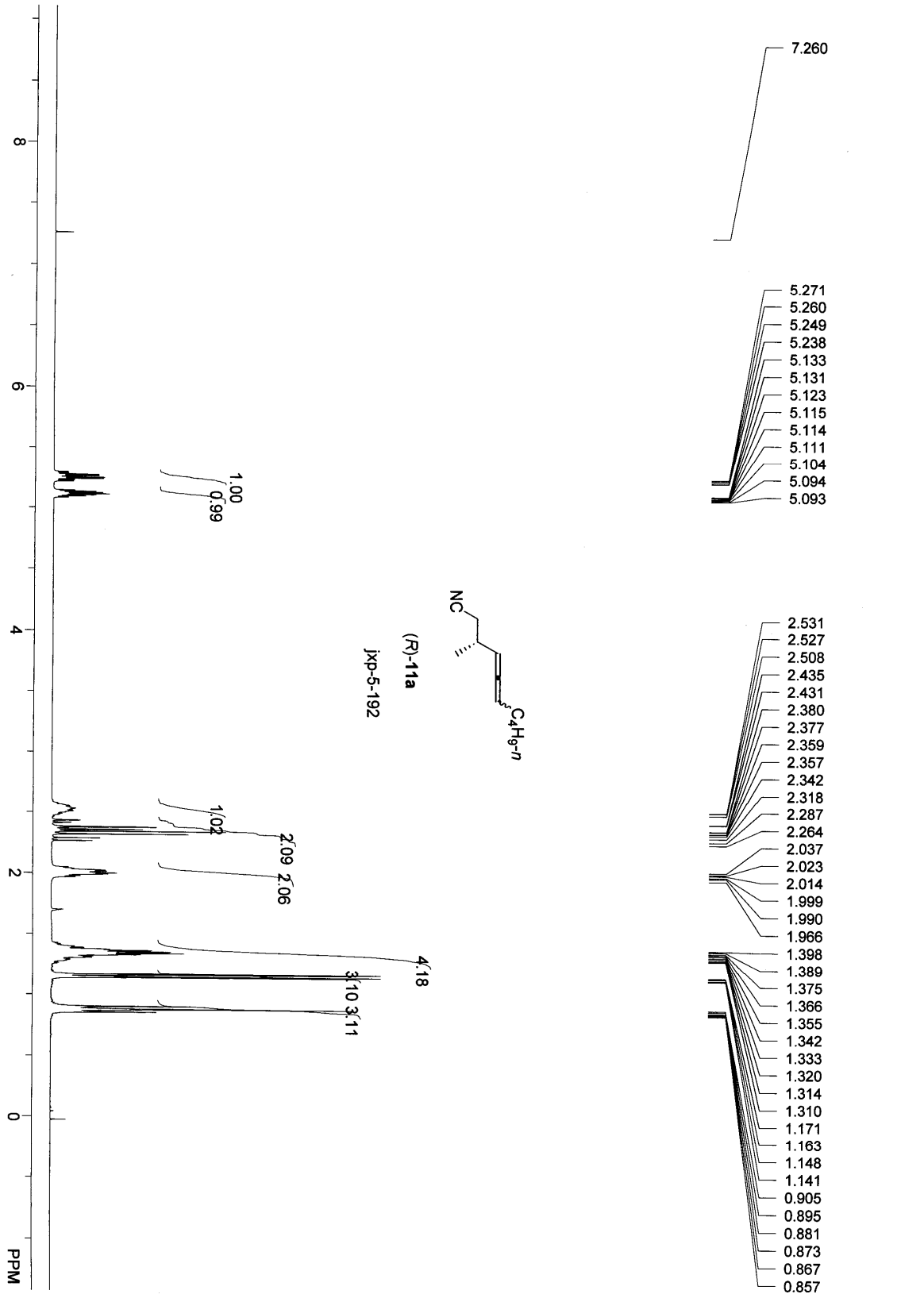
2.03
1.04
4.34
3.08
3.23
9.20
0 PPM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5.260
5.249
5.238
5.133
5.131
5.123
5.115
5.114
5.111
5.104
5.094
5.093
2.531
2.527
2.508
2.435
2.431
2.380
2.377
2.359
2.357
2.342
2.318
2.287
2.264
2.037
2.023
2.014
1.999
1.990
1.966
1.398
1.389
1.375
1.366
1.355
1.342
1.333
1.320
1.314
1.310
1.171
1.163
1.148
1.141
0.905
0.895
0.881
0.873
0.867
0.857
1.00
0.99
1.02
2.09
2.06
4.18
3.10
3.11
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C4H9-n
(R)-11a
jxp-5-192
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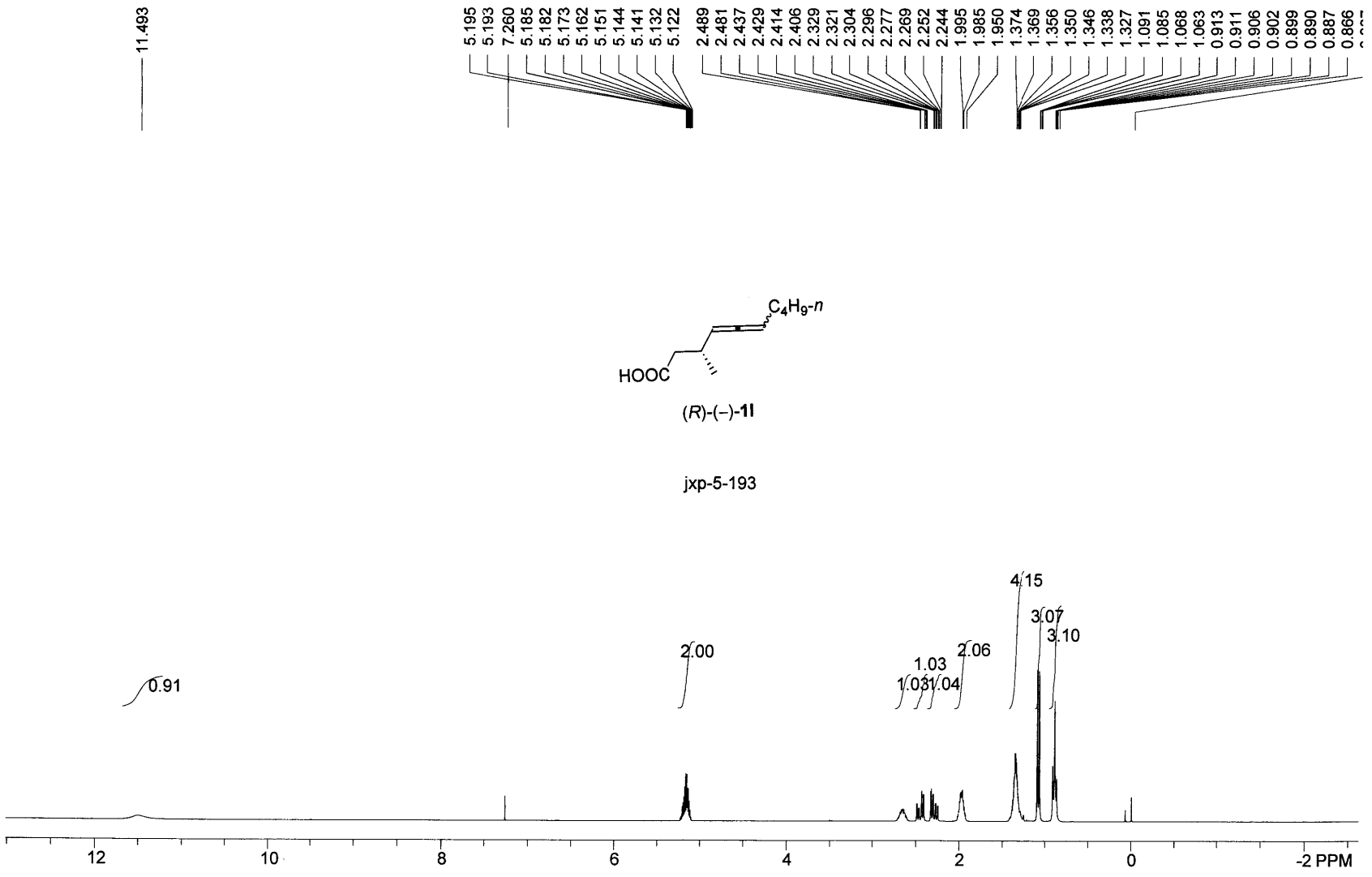
6
4
2
0
PPM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5.182
5.173
5.162
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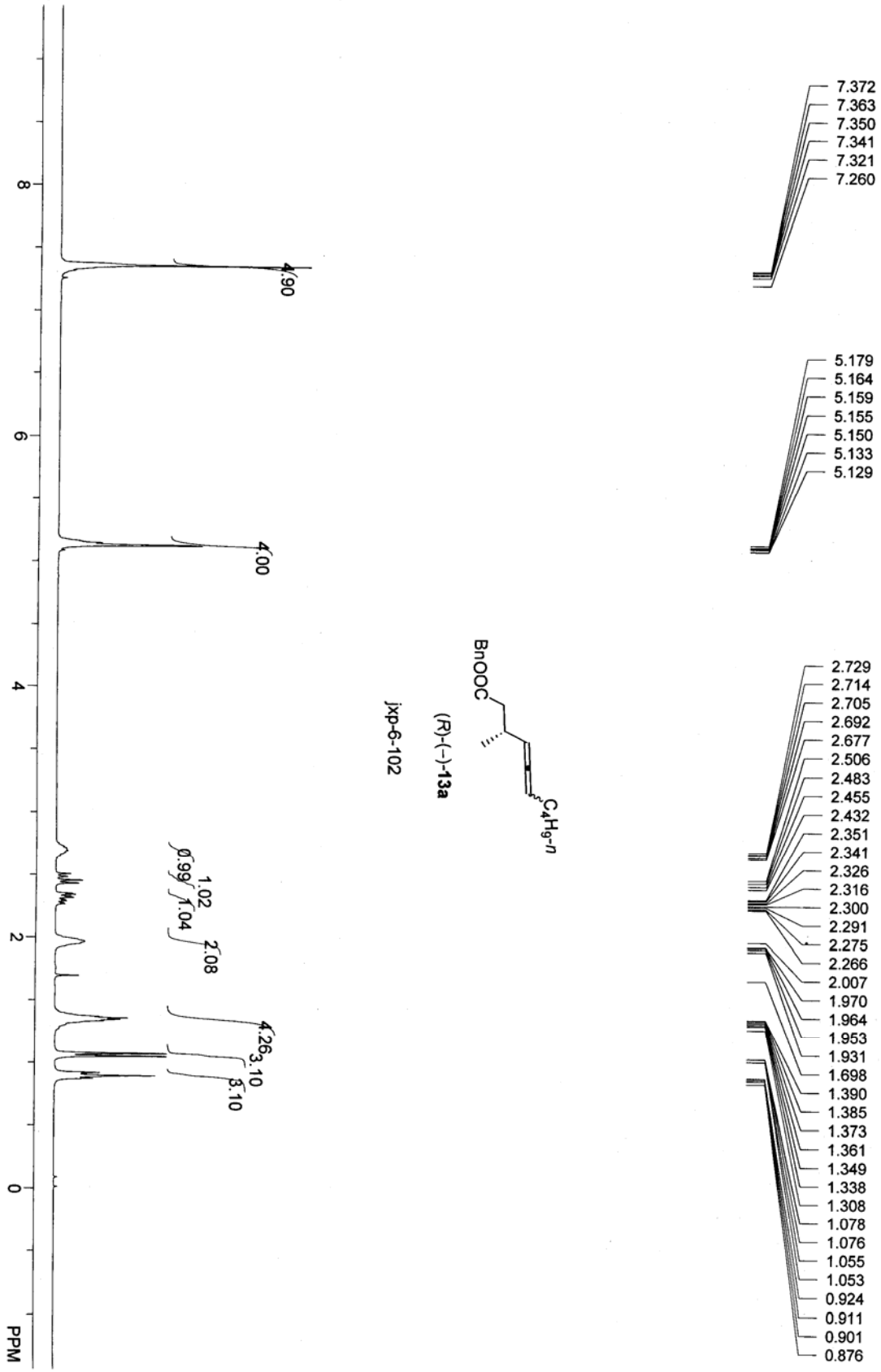
5.144
5.141
5.132
5.122
2.489
2.481
2.437
2.429
2.414
2.406
2.329
2.321
2.304
2.296
2.277
2.269
2.252
2.244
1.995
1.985
1.950
1.374
1.369
1.356
1.350
1.346
1.338
1.327
1.091
1.085
1.068
1.063
0.913
0.911
0.906
0.902
0.899
0.890
0.887
0.866
C4H9-n
HOOC
(R)-(−)-1l
jxp-5-193
0.91
2.00
1.03
1.03
1.04
2.06
4.15
3.07
3.10
12
10
8
6
4
2
0
-2 PPM


7.372
7.363
7.350
7.341
7.321
7.260
5.179
5.164
5.159
5.155
5.150
5.133
5.129
2.729
2.714
2.705
2.692
2.677
2.506
2.483
2.455
2.432
2.351
2.341
2.326
2.316
2.300
2.291
2.275
2.266
2.007
1.970
1.964
1.953
1.931
1.698
1.390
1.385
1.373
1.361
1.349
1.338
1.308
1.078
1.076
1.055
1.053
0.924
0.911
0.901
0.876
BnOOC
C4H9-n
(R)-(−)-13a
jxp-6-102
4.90
4.00
1.02
0.99
1.04
2.08
4.26
3.10
3.10
8
6
4
2
0
PPM

The two isomers (S_a, *R*)-(+)-**13a** and (R_a, *R*)-(–)-**13a** were separated from (*R*)-(–)-**13a** by using CHIRALPAK IC column.

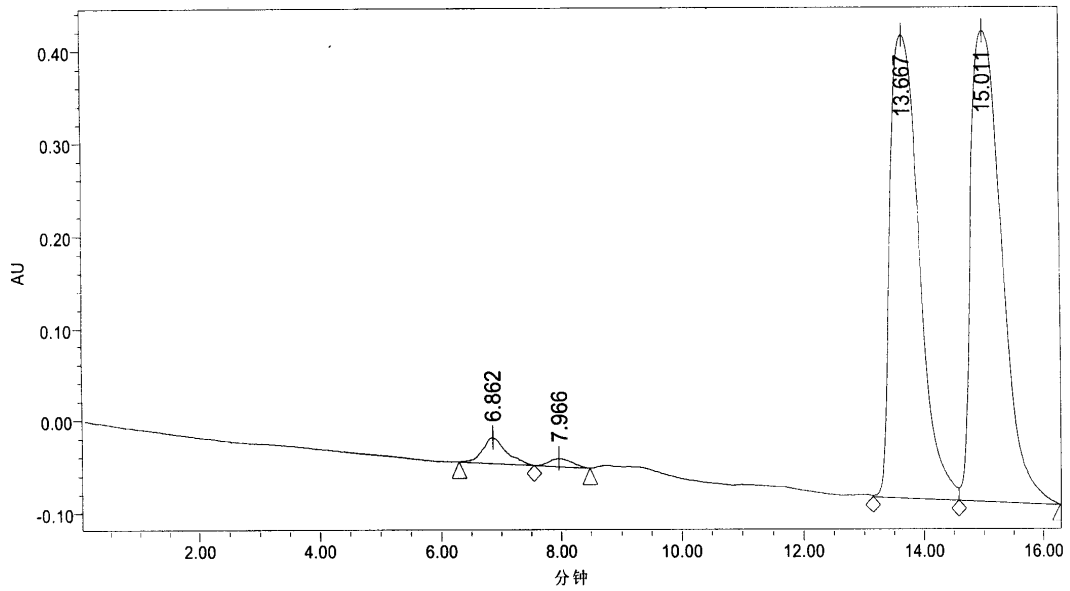
Default Result LC 报告

用户名称：System　　项目名称：Defaults

样品信息

样品名称:	jxp-test5	采集者:	System
样品类型:	未知	采集时间:	2008-6-4 下午 07:06:21
瓶号:	1	采集方法组:	uv01
进样次数:	10	处理日期:	2008-6-6 下午 03:44:54
进样体积:	~~10.00 ul~~ 2ml 1mg/ml	处理方法:	Default
运行时间:	100.0 Minutes	通道名称:	2487通道 1
样品组名称:		处理通道注释:	

自动标尺色谱图

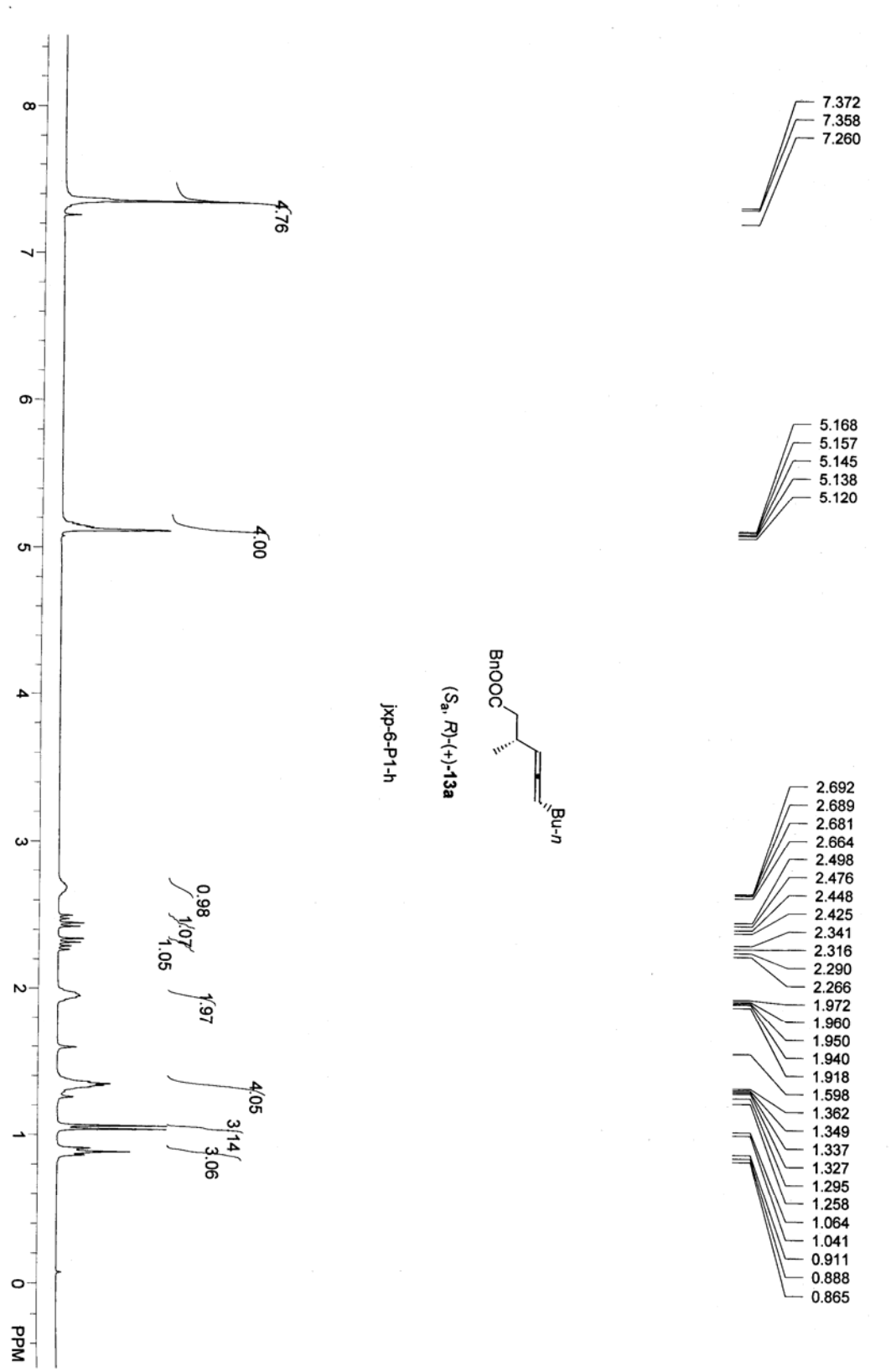


色谱峰结果

	名字	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		6.862	757700	27818	2.11
2		7.966	229769	8471	0.64
3		13.667	16647075	499387	46.35
4		15.011	18283400	507880	50.90

报告方法：Default Result LC　　打印 下午 03:45:30　2008-6-6　　页码：1 (共计 1)

The ^{1}H NMR spectrum of (S_a, *R*)-(+)-**13a** separated from (*R*)-(–)-**13a** by using CHIRALPAK IC column.

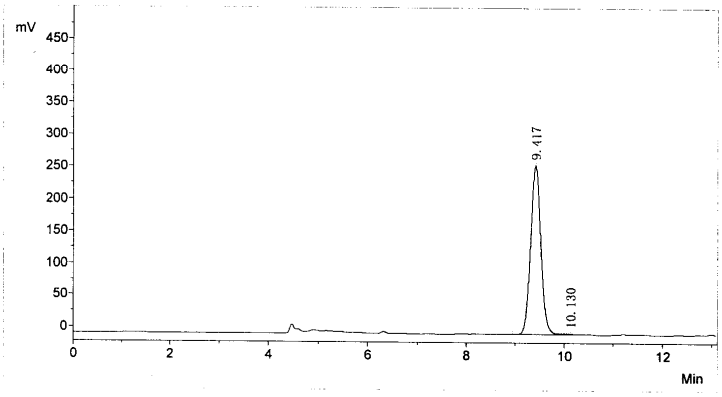


The HPLC spectrum of of (S_a, *R*)-(+)-**13a**

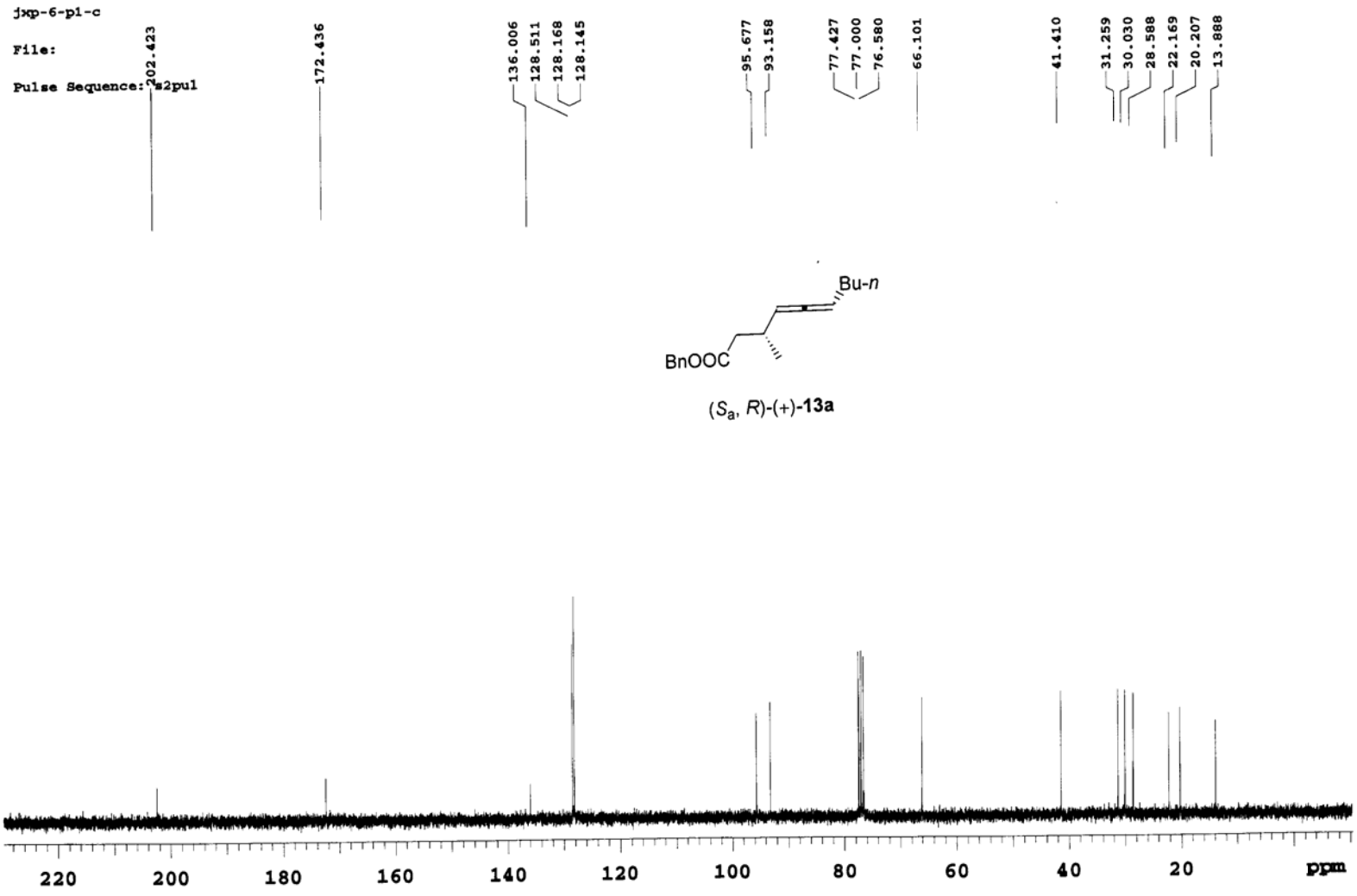
HPLC REPORT

Sample Name:jxp-6-pl.che
Time:12:50
Column: OJ-H
Wave Length: 214nm

Date:2008-06-06
Method:
Flow Rate: 0.7ml/min
Mobile Phase: n-hex/i-proy = 99/1



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	9.417	262363.2	3821561.6	99.5026
2	2	Unknown	10.130	719.1	19105.0	0.4974
Total				263082.2	3840666.6	100.0000


jxp-6-pi-c
File:
Pulse Sequence: s2pul
202.423
172.436
136.006
128.511
128.168
128.145
95.677
93.158
77.427
77.000
76.580
66.101
41.410
31.259
30.030
28.588
22.169
20.207
13.888
Bu-n
BnOOC
220
200
180
160
140
120
100
80
60
40
20
ppm

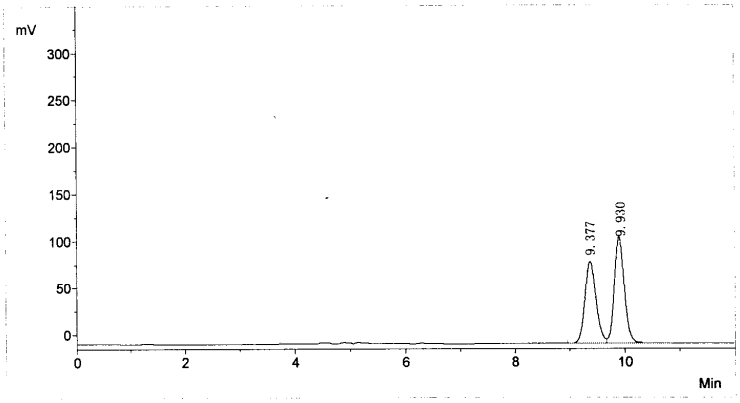
(S_a, *R*)-(+)-**13a**

The HPLC spectrum of (*R*)-(–)-**13a**

HPLC REPORT

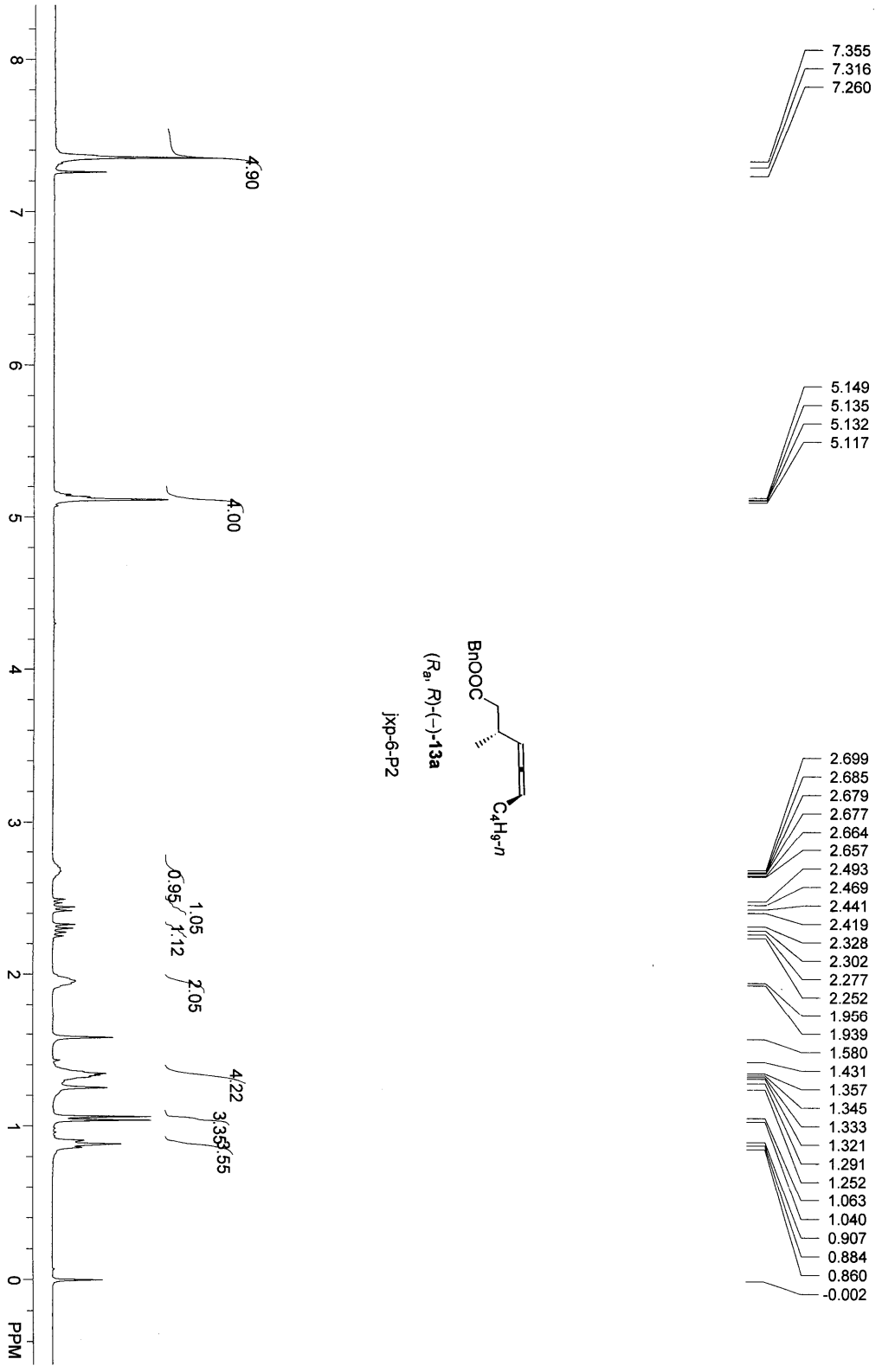
Sample Name: jxp-6-102..che
Time: 12:37
Column: OJ-H
Wave Length: 214 nm

Date: 2008-06-06
Method:
Flow Rate: 0.7 ml/min
Mobile Phase: n-hex/i-prOH = 99/1



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	9.377	87565.7	1231206.4	46.3814
2	2	Unknown	9.930	106973.3	1423320.3	53.6186
Total				194539.0	2654526.6	100.0000

The ^{1}H NMR spectrum of (R_a, *R*)-(–)-**13a** separated from (*R*)-(–)-**13a** by using CHIRALPAK IC column.

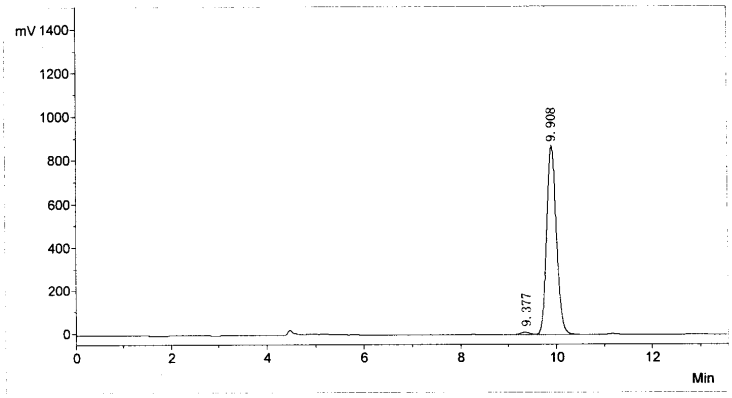


The HPLC spectrum of (R_a, *R*)-(–)-**13a**

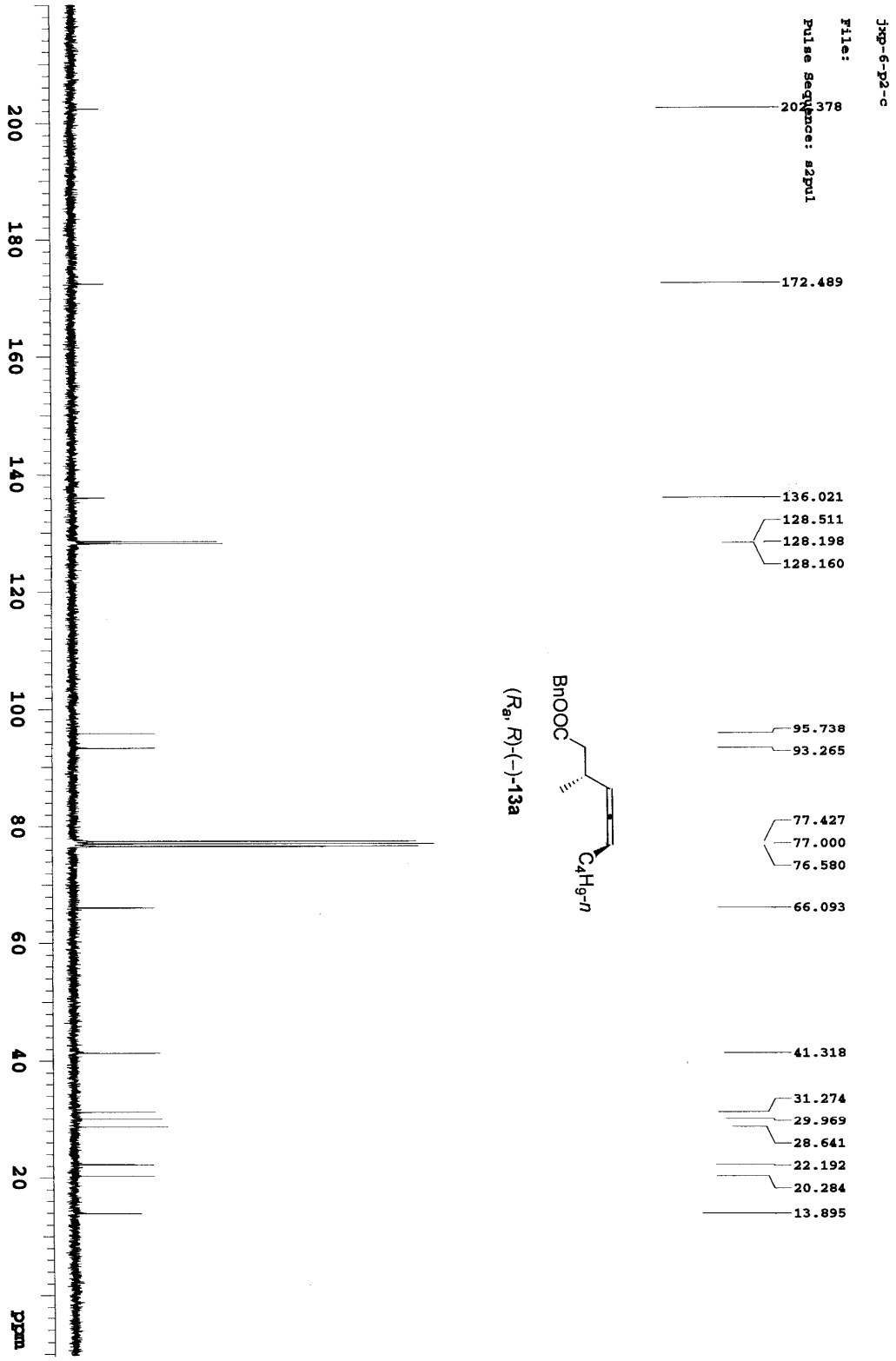
HPLC REPORT

Sample Name: jxp-6-p2.che
Time: 13:04
Column: OJ-H
Wave Length: 214nm

Date: 2008-06-06
Method:
Flow Rate: 0.7ml/min
Mobile Phase: n-hexane-IPOH=99/1



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	9.377	9994.7	162961.6	1.3041
2	2	Unknown	9.908	862100.6	12332896.3	98.6959
Total				872095.3	12495857.9	100.0000


jsp-6-p2-c
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Pulse Sequence: s2pul
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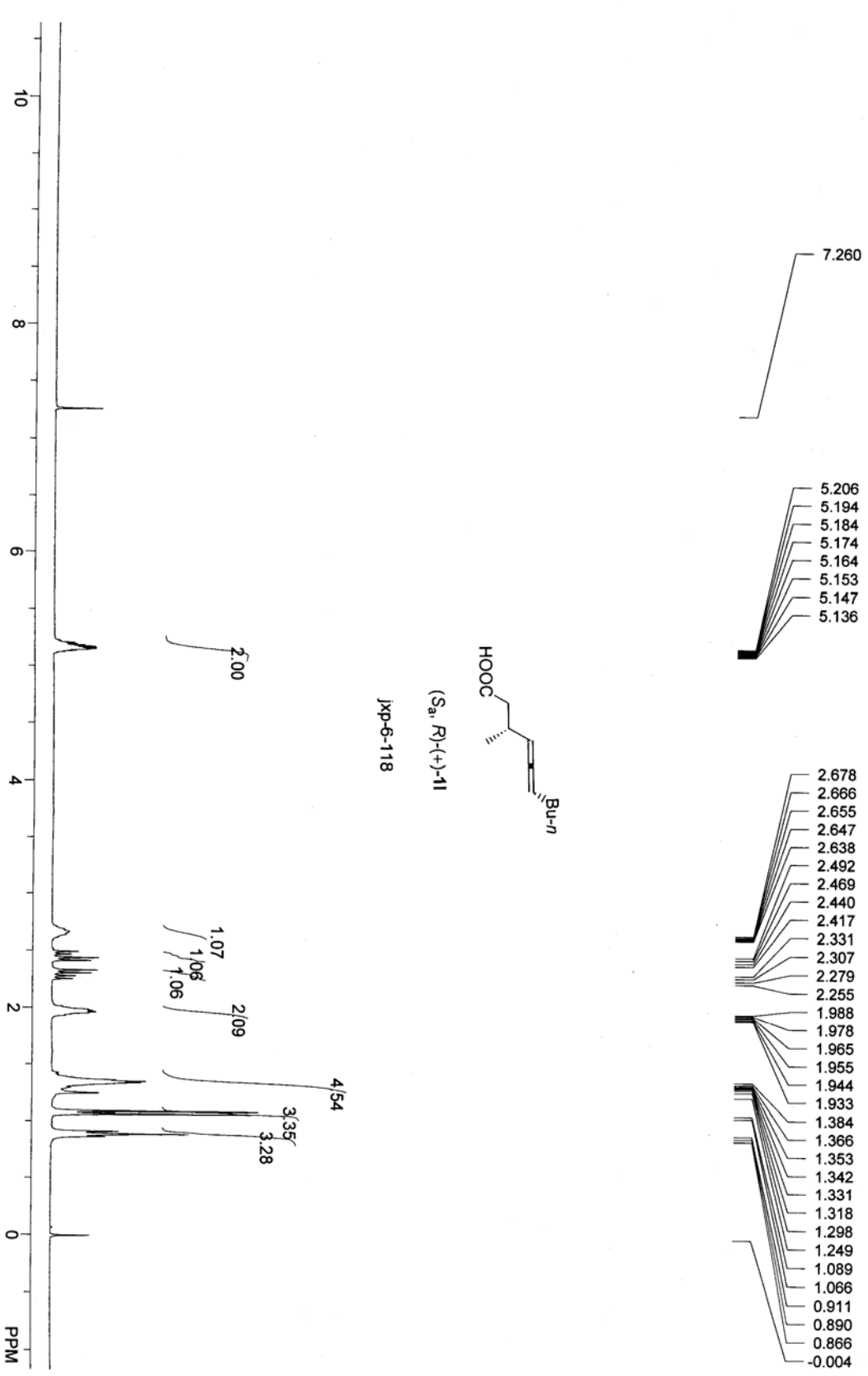
77.000
76.580
66.093
41.318
31.274
29.969
28.641
22.192
20.284
13.895
BnOOC
C4H9-n
(Ra, R)-(−)-13a
200
180
160
140
120
100
80
60
40
20
ppm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5.164
5.153
5.147
5.136
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2.666
2.655
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2.638
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2.469
2.440
2.417
2.331
2.307
2.279
2.255
1.988
1.978
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1.955
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1.366
1.353
1.342
1.331
1.318
1.298
1.249
1.089
1.066
0.911
0.890
0.866
-0.004
HOOC
Bu-n
(Sa, R)-(+)-1l
jxp-6-118
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1.06
2.09
4.54
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10
8
6
4
2
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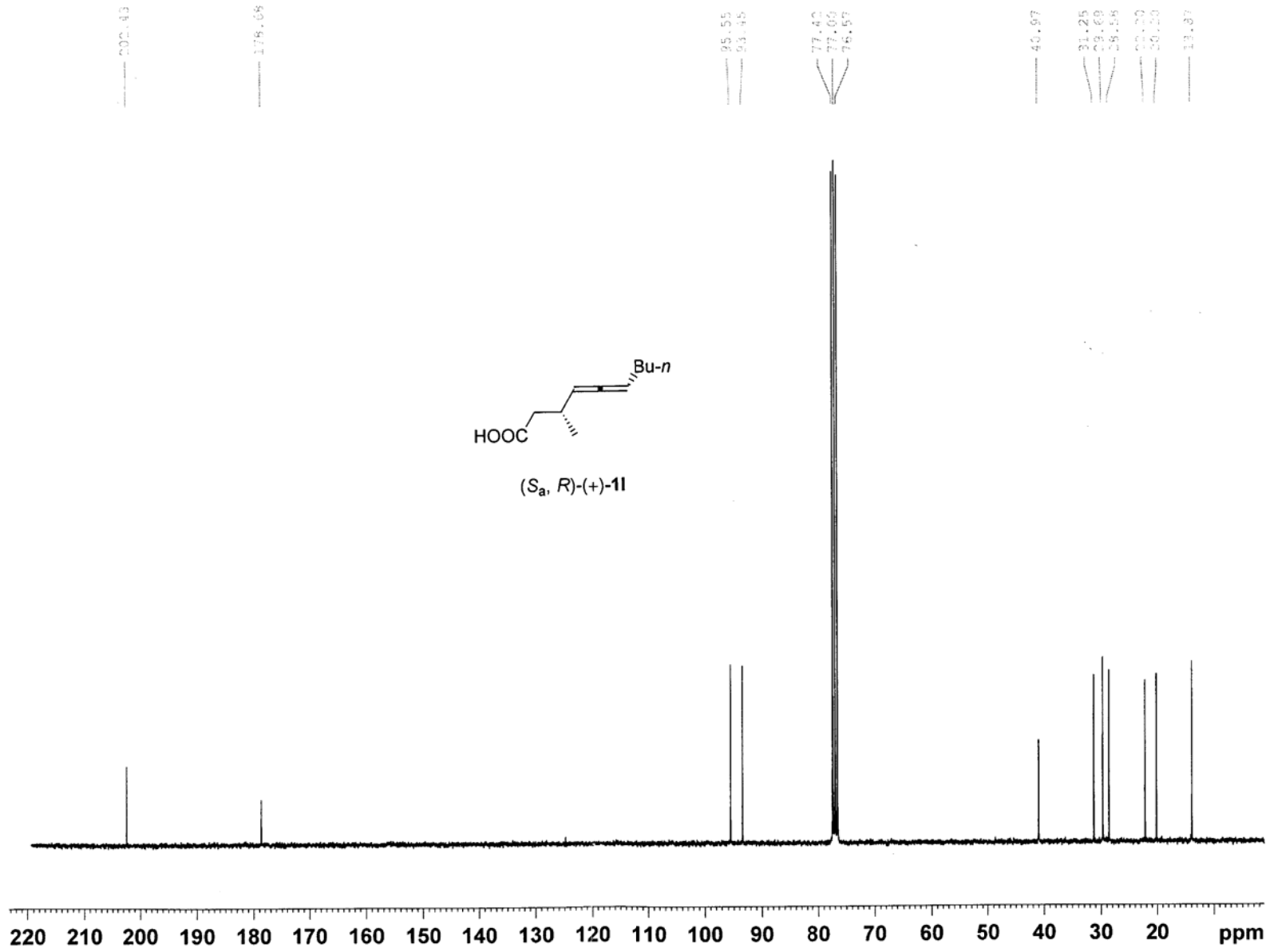
PPM


202.43
176.66
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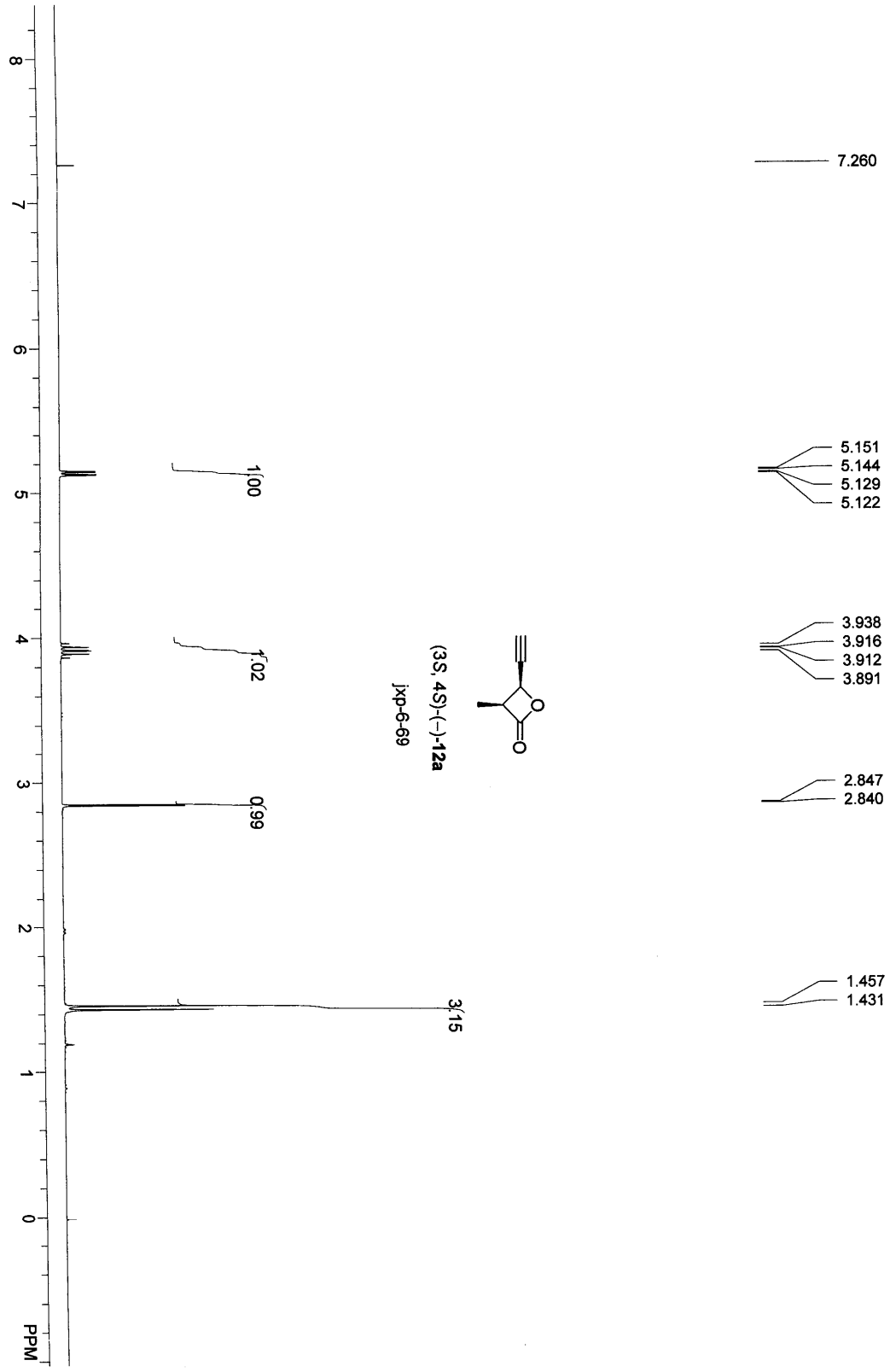
77.42
77.00
76.57
40.97
31.25
29.69
28.56
22.32
20.20
13.37
Bu-n
HOOC
(Sa, R)-(+)-1l
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.260
5.151
5.144
5.129
5.122
3.938
3.916
3.912
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2.847
2.840
1.457
1.431
1.00
1.02
0.99
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(3S, 4S)-(−)-12a
jxp-6-69
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O
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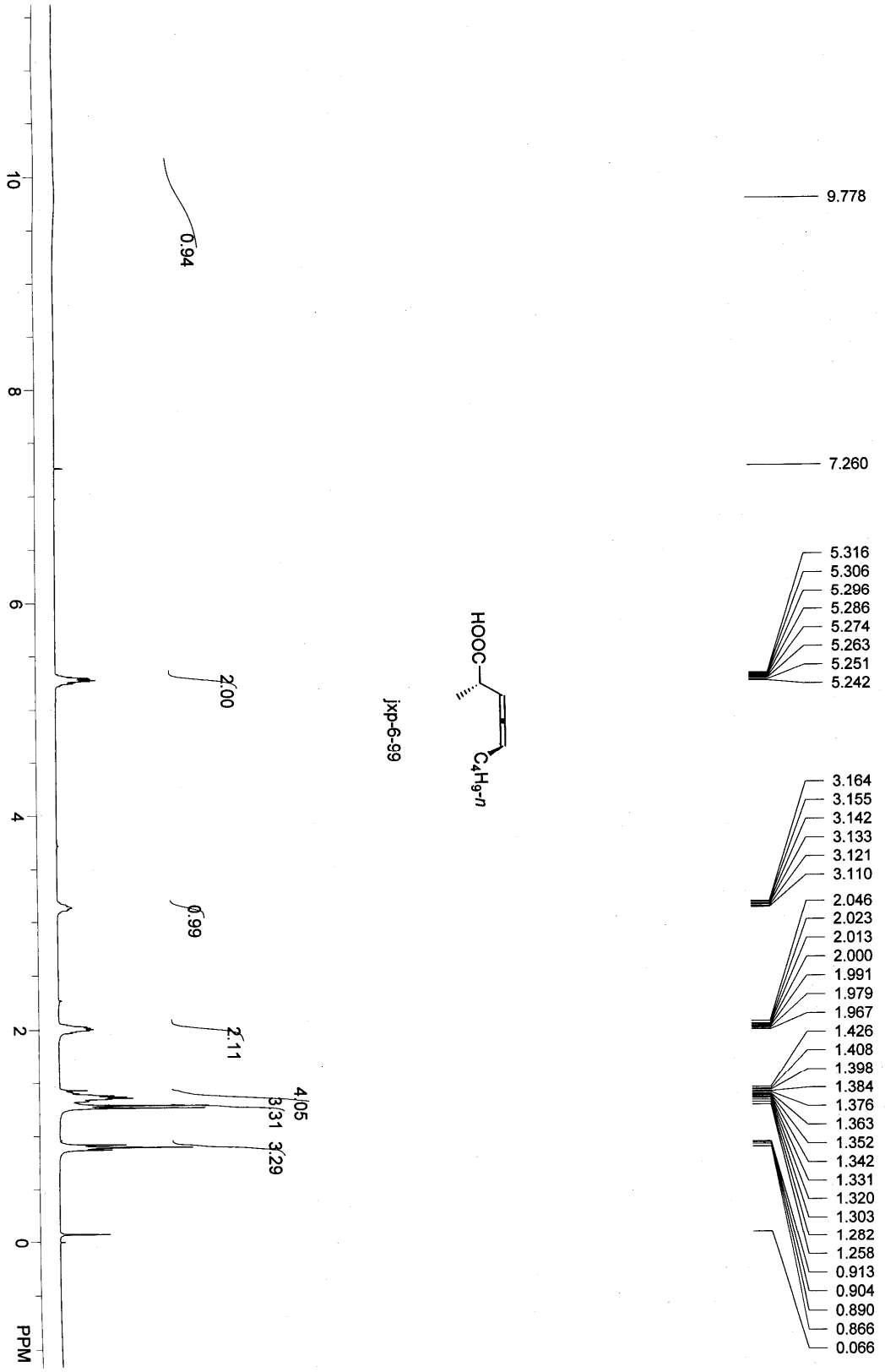
PPM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5.242
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3.142
3.133
3.121
3.110
2.046
2.023
2.013
2.000
1.991
1.979
1.967
1.426
1.408
1.398
1.384
1.376
1.363
1.352
1.342
1.331
1.320
1.303
1.282
1.258
0.913
0.904
0.890
0.866
0.066
HOOC
C_4H_9-n
jxp-6-99
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10
8
6
4
2
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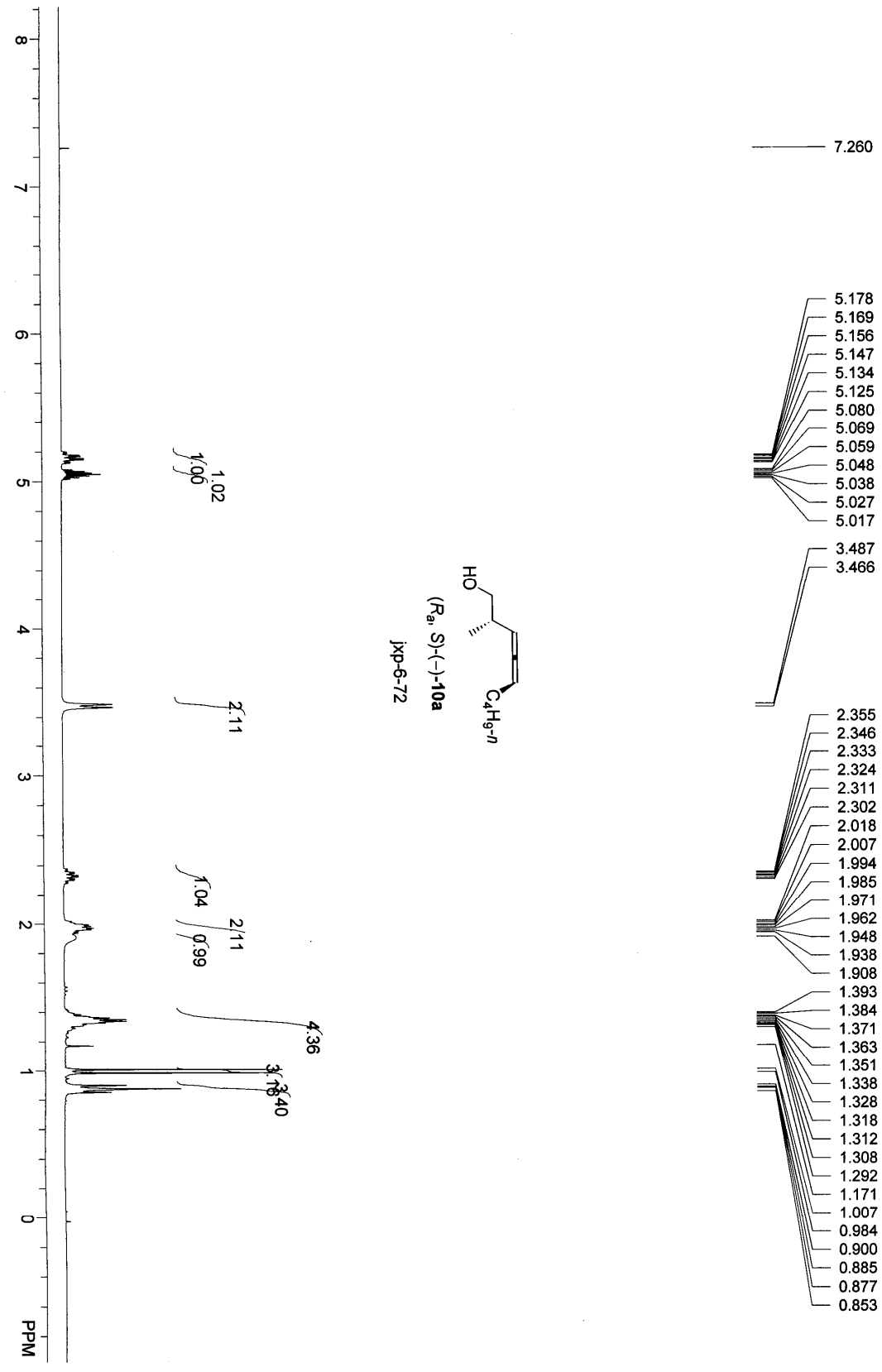
PPM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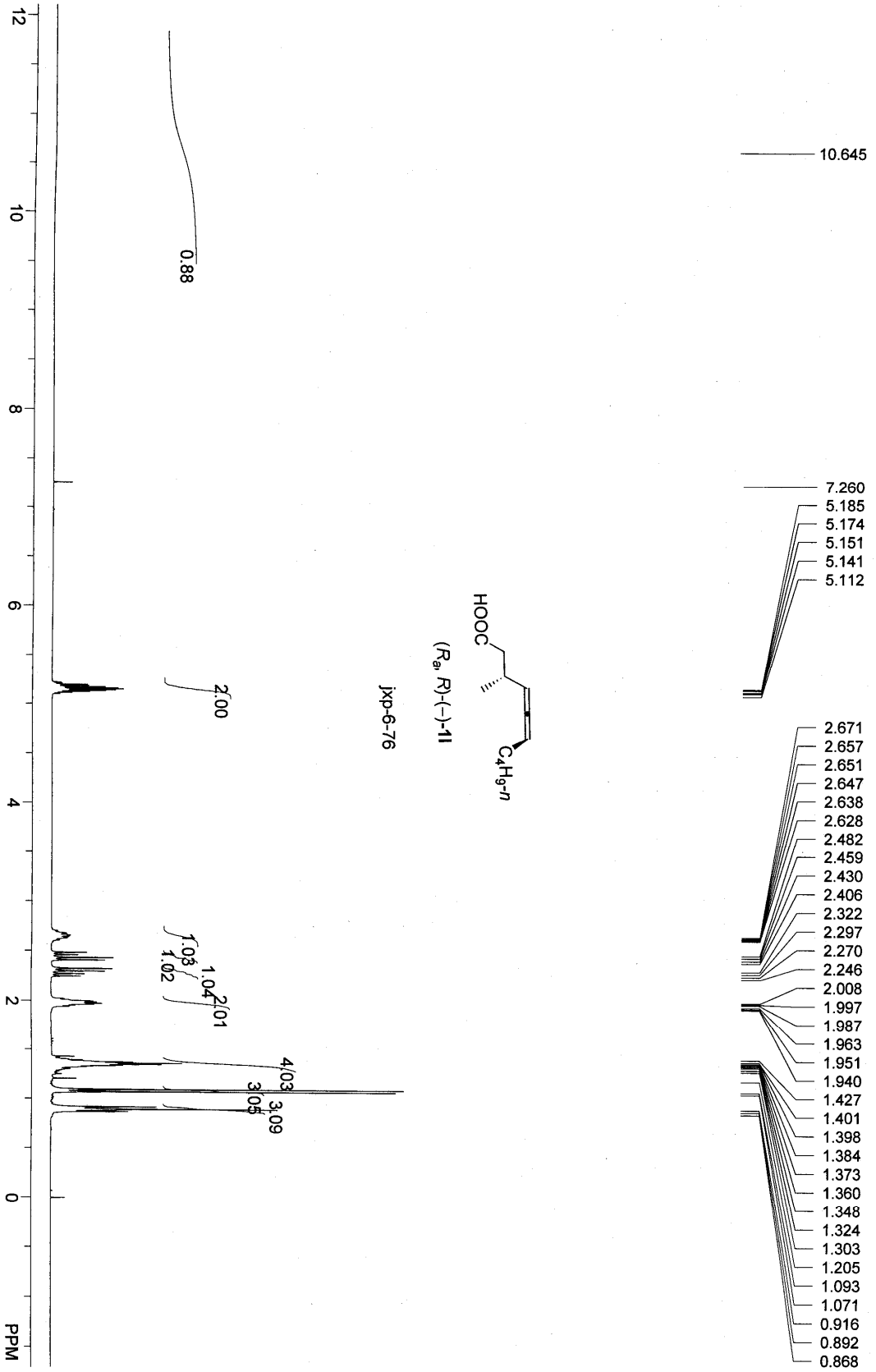
5.080
5.069
5.059
5.048
5.038
5.027
5.017
3.487
3.466
2.355
2.346
2.333
2.324
2.311
2.302
2.018
2.007
1.994
1.985
1.971
1.962
1.948
1.938
1.908
1.393
1.384
1.371
1.363
1.351
1.338
1.328
1.318
1.312
1.308
1.292
1.171
1.007
0.984
0.900
0.885
0.877
0.853
HO
C4H9-n
(Ra, S)-(−)-10a
jxp-6-72
1.02
1.00
2.11
1.04
0.99
2.11
4.36
3.40
PPM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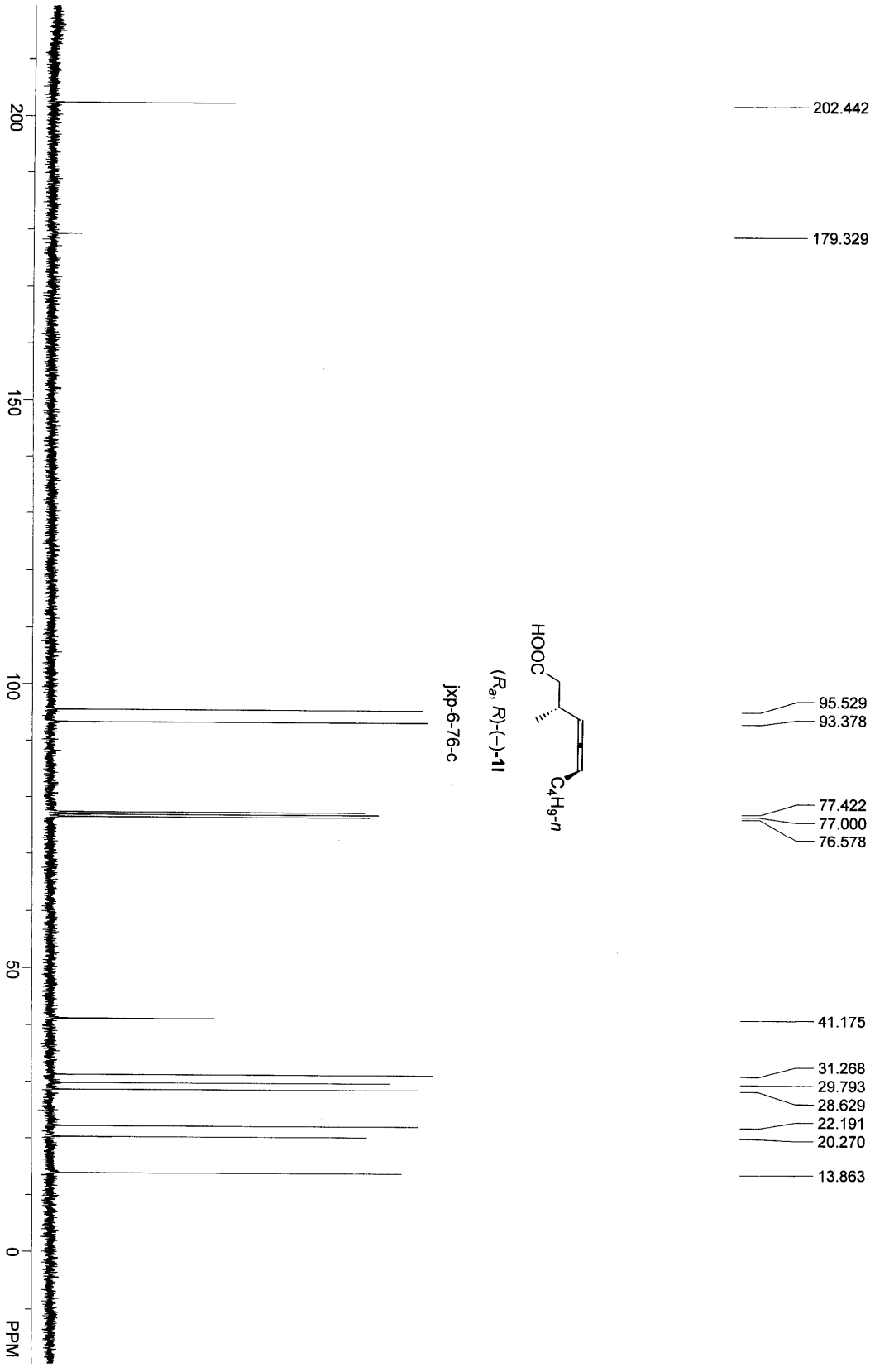
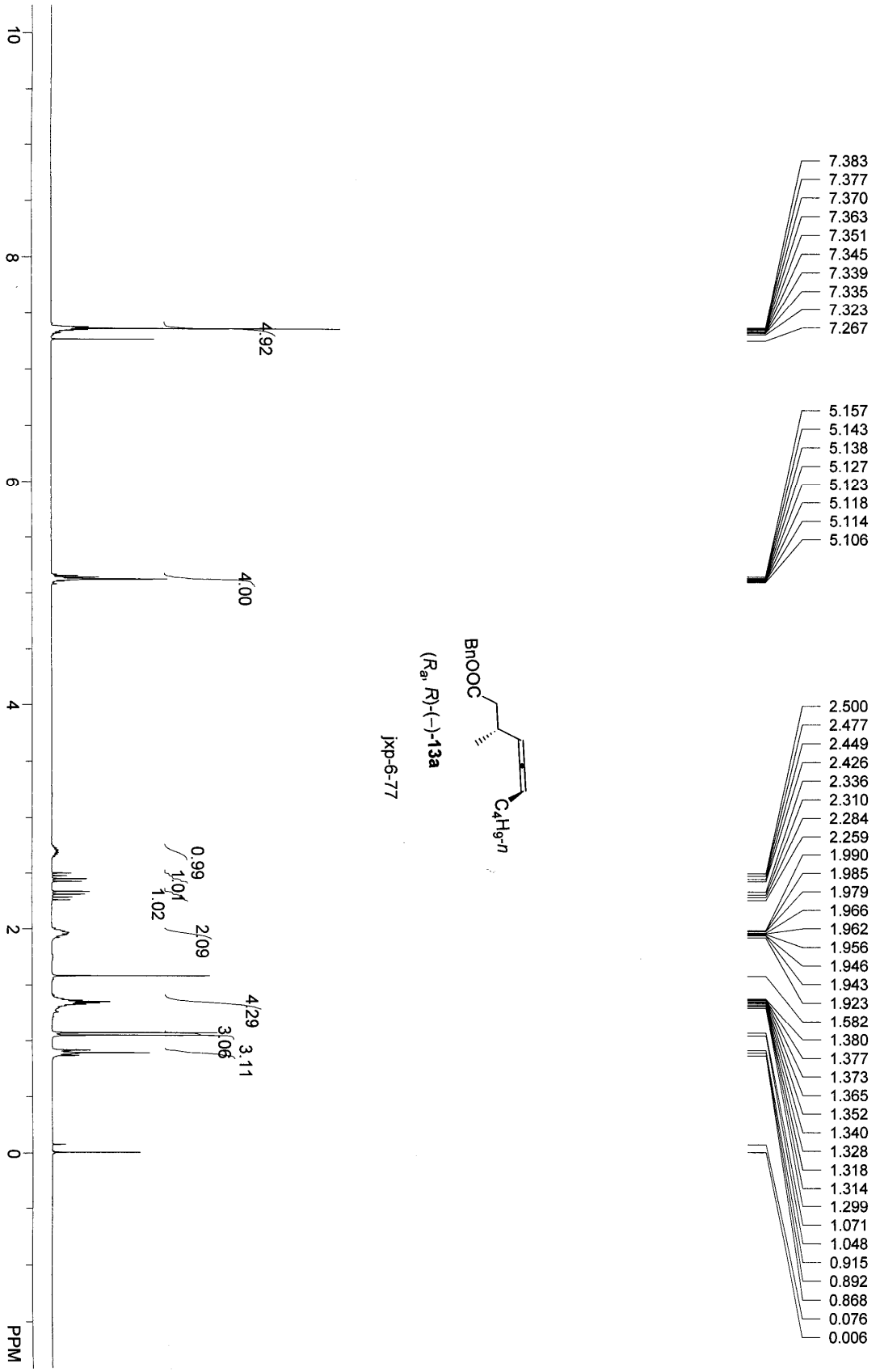
7.260
5.185
5.174
5.151
5.141
5.112
2.671
2.657
2.651
2.647
2.638
2.628
2.482
2.459
2.430
2.406
2.322
2.297
2.270
2.246
2.008
1.997
1.987
1.963
1.951
1.940
1.427
1.401
1.398
1.384
1.373
1.360
1.348
1.324
1.303
1.205
1.093
1.071
0.916
0.892
0.868
HOOC
C4H9-n
(Ra, R)-(−)-11
jxp-6-76
0.88
2.00
1.03
1.02
1.04
2.01
4.03
3.05
3.09
12
10
8
6
4
2
0
PPM


200
150
100
50
0
PPM
202.442
179.329
95.529
93.378
77.422
77.000
76.578
41.175
31.268
29.793
28.629
22.191
20.270
13.863
HOOC
C4H9-n
(Ra, R)-(−)-1l
jxp-6-76-c


7.383
7.377
7.370
7.363
7.351
7.345
7.339
7.335
7.323
7.267
5.157
5.143
5.138
5.127
5.123
5.118
5.114
5.106
2.500
2.477
2.449
2.426
2.336
2.310
2.284
2.259
1.990
1.985
1.979
1.966
1.962
1.956
1.946
1.943
1.923
1.582
1.380
1.377
1.373
1.365
1.352
1.340
1.328
1.318
1.314
1.299
1.071
1.048
0.915
0.892
0.868
0.076
0.006
BnOOC
C_4H_9-n
(R_a, R)-(−)-**13a**
jxp-6-77
4.92
4.00
0.99
1.01
1.02
2.09
4.29
3.06
3.11
10
8
6
4
2
0
PPM

The HPLC spectrum of (R_a, *R*)-(–)-**13a**

Data File D:\HPCHEM\1\DATA\JXP\JXP00235.D Sample Name: jxp-6-77-sx

n-hexane/i-propanol=99/1; 214nm; 0.5ml/min; OJ-H

```
==========================================================================
Injection Date  : 5/1/2008 1:25:26 PM
Sample Name     : jxp-6-77-sx                    Location :   -
Acq. Operator   : jxp
Method          : D:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 5/1/2008 1:08:56 PM by jxp
                  (modified after loading)
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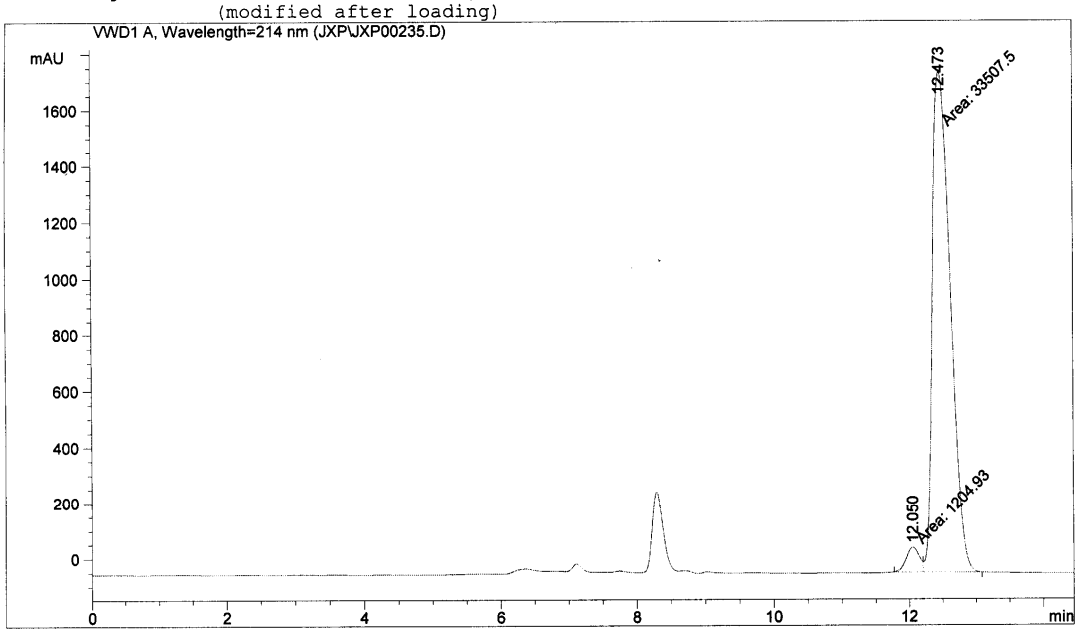


```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=214 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  12.050 MF    0.2252 1204.93018   89.18591   3.4712
   2  12.473 FM    0.3130 3.35075e4  1784.00562  96.5288

Totals :                  3.47124e4  1873.19153

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Instrument 1 5/1/2008 2:02:24 PM jxp Page 1 of 1

The HPLC spectrum of (*R*)-(–)-**13a**

Data File D:\HPCHEM\1\DATA\JXP\JXP00237.D

Sample Name: jxp-6-30-wx

n-hexane/i-propanol=99/1; 214nm; 0.5ml/min; OJ-H

```
==========================================================================
Injection Date  : 5/1/2008 2:00:21 PM
Sample Name     : jxp-6-30-wx                    Location :   -
Acq. Operator   : jxp
Acq. Method     : D:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 5/1/2008 1:08:56 PM by jxp
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Analysis Method : D:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 5/1/2008 2:14:13 PM by jxp
                  (modified after loading)
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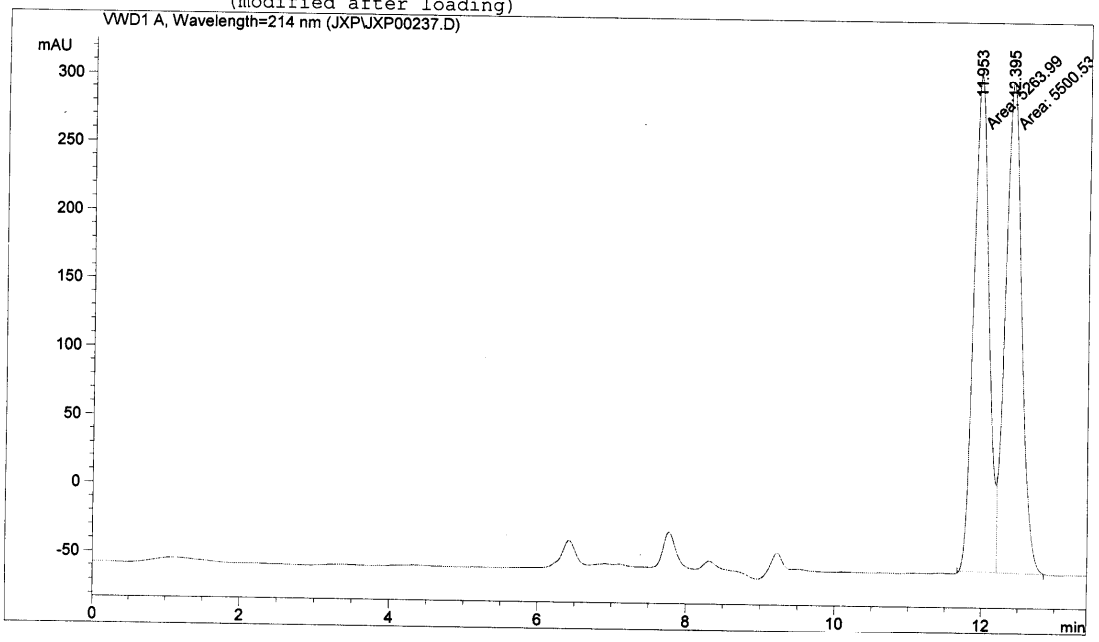



```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=214 nm

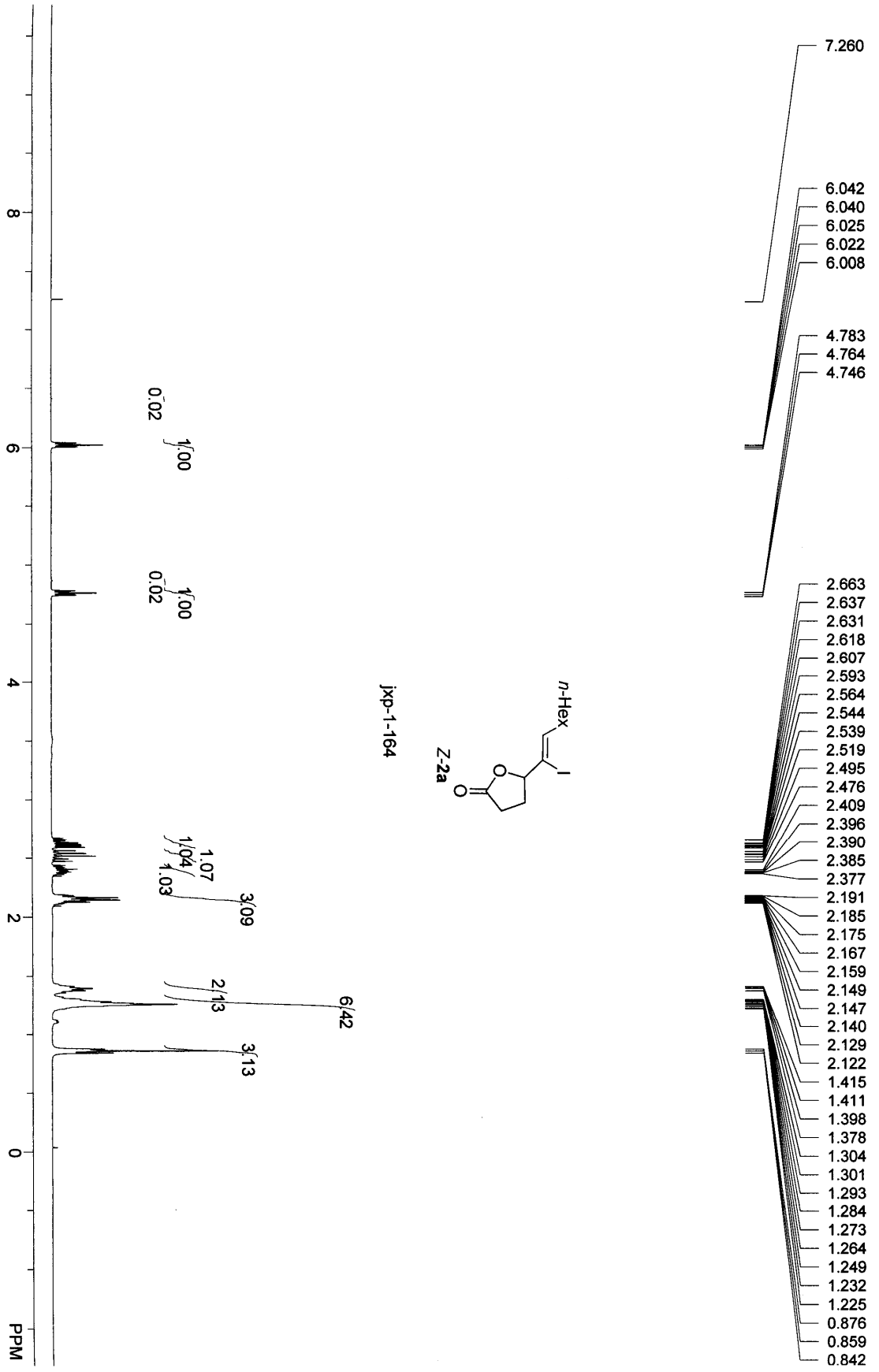
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  11.953 MF    0.2415 5263.98975  363.28394  48.9013
   2  12.395 FM    0.2559 5500.52783  358.18600  51.0987

Totals :                  1.07645e4   721.46994

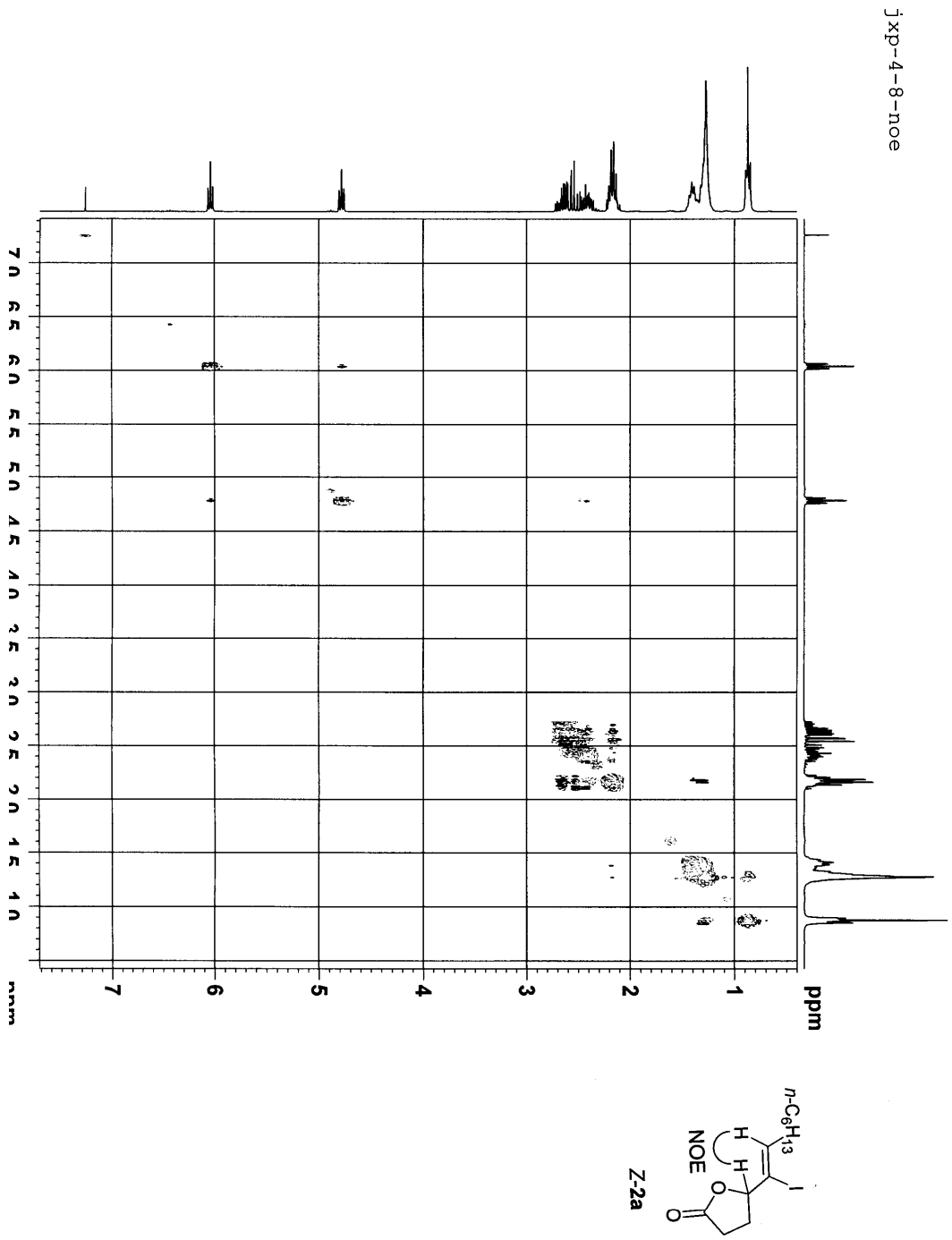
 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

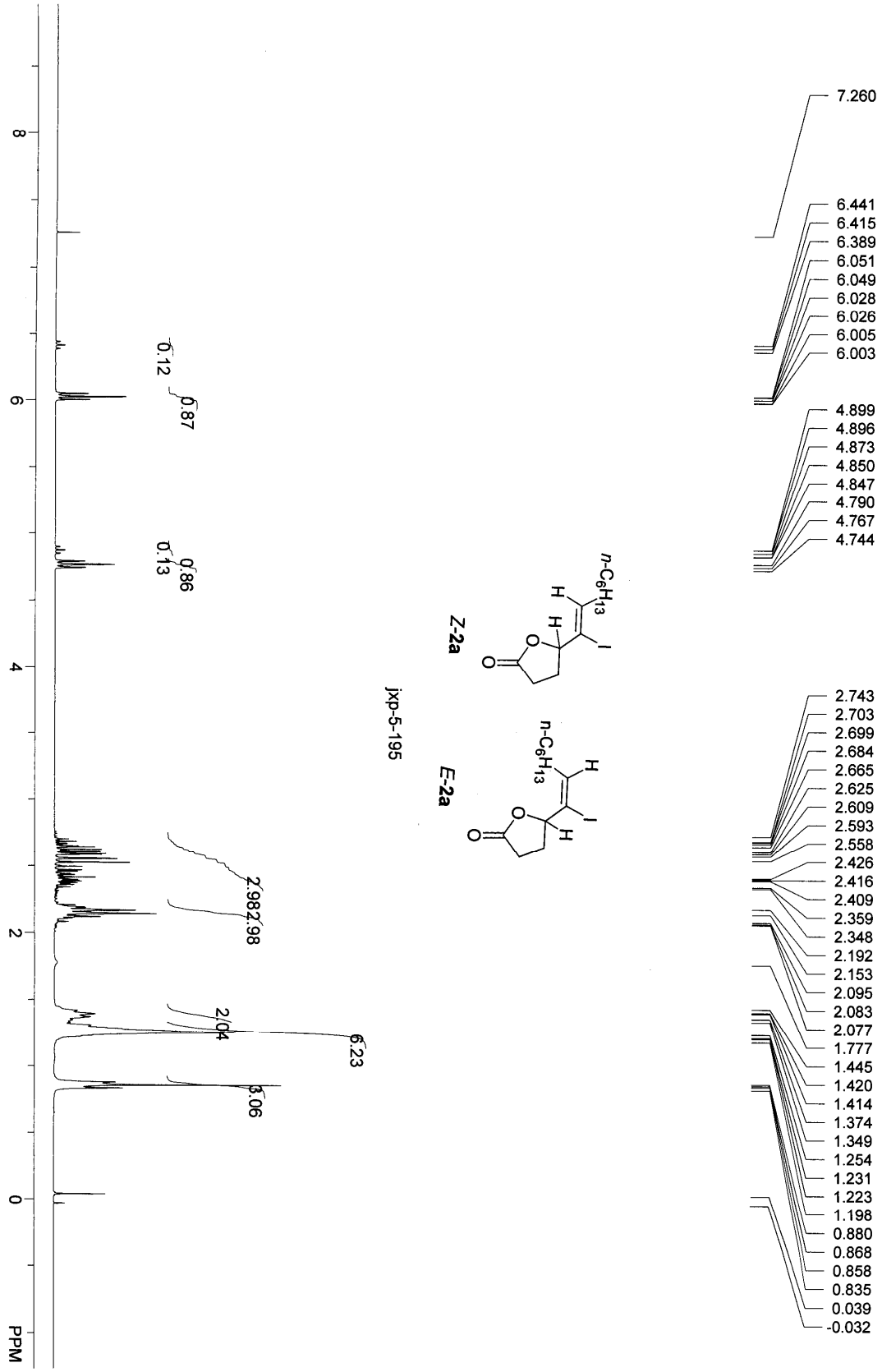
Instrument 1 5/1/2008 2:37:54 PM jxp

Page 1 of 1

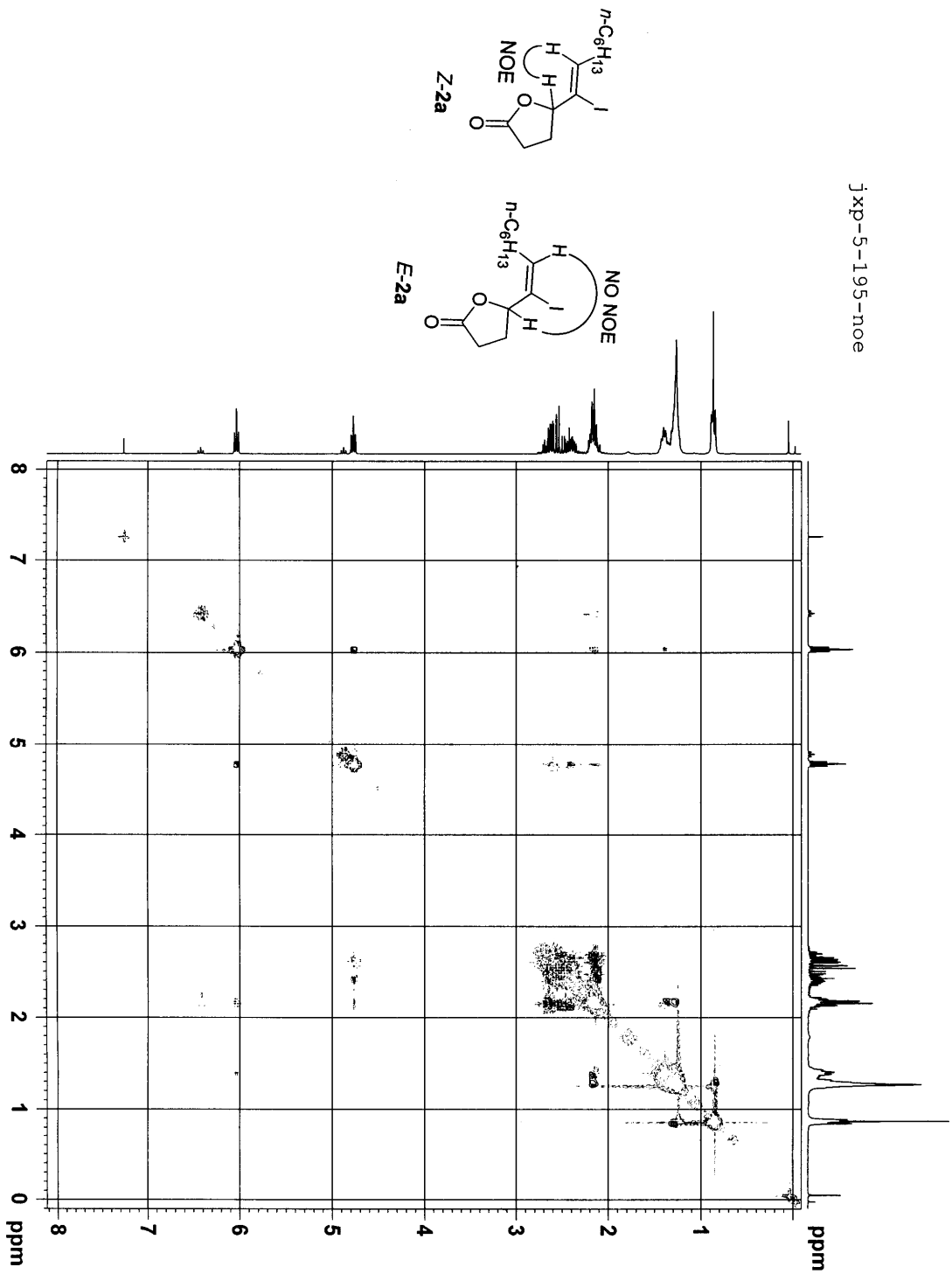

7.260
6.042
6.040
6.025
6.022
6.008
4.783
4.764
4.746
2.663
2.637
2.631
2.618
2.607
2.593
2.564
2.544
2.539
2.519
2.495
2.476
2.409
2.396
2.390
2.385
2.377
2.191
2.185
2.175
2.167
2.159
2.149
2.147
2.140
2.129
2.122
1.415
1.411
1.398
1.378
1.304
1.301
1.293
1.284
1.273
1.264
1.249
1.232
1.225
0.876
0.859
0.842
n-Hex
I
O
O
Z-2a
jxp-1-164
0.02
1.00
0.02
1.00
1.07
1.04
1.03
3.09
2.13
6.42
3.13
8
6
4
2
0
PPM

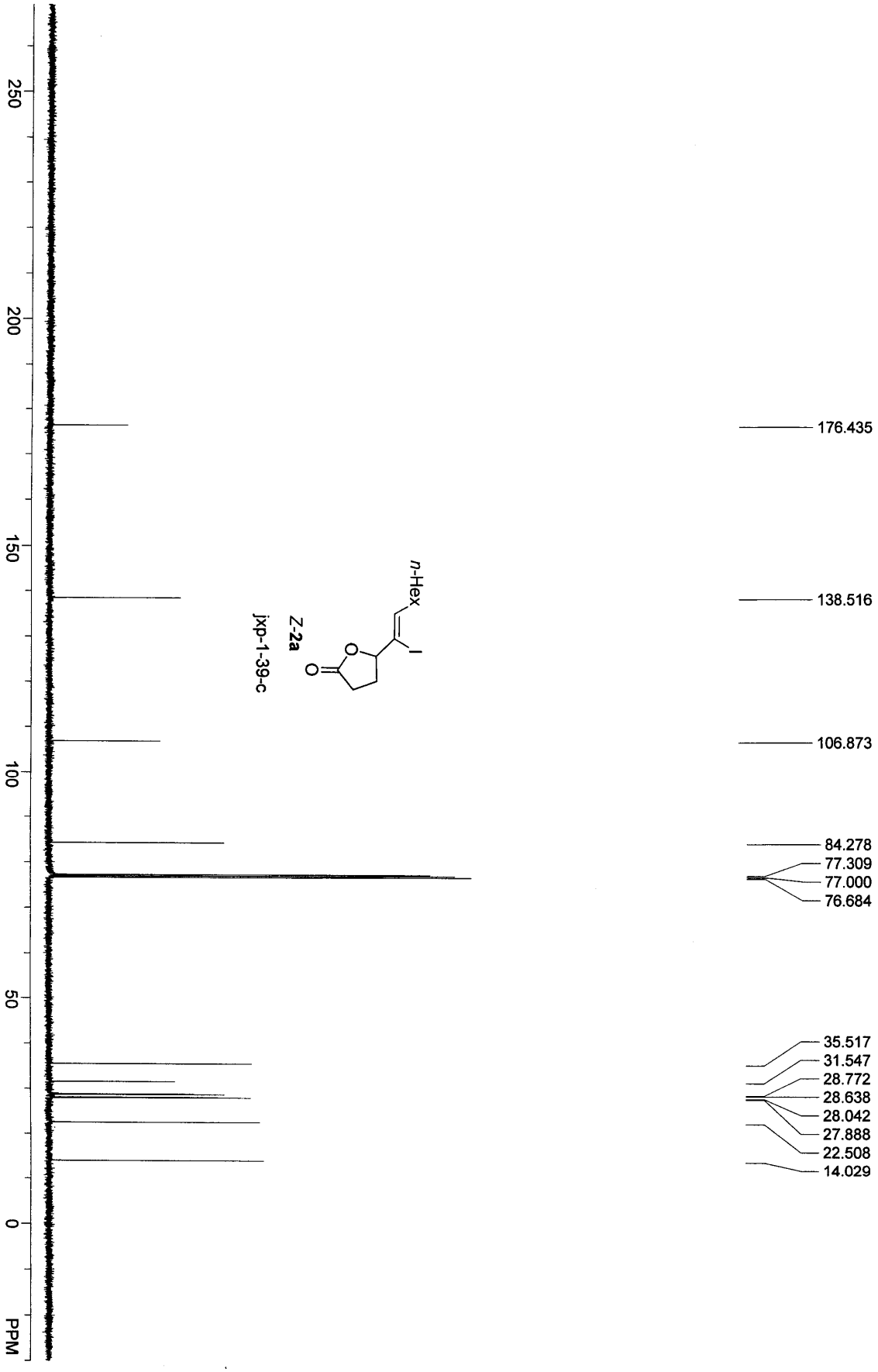
NOESY spectrum of *Z*-**2a**

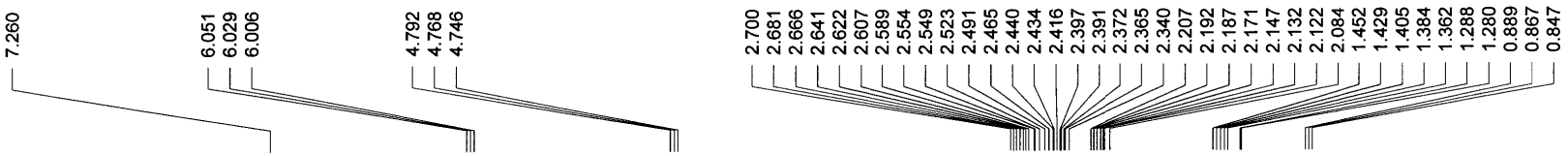


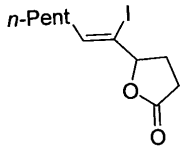


NOESY spectrum of *Z*-**2a** and *E*-**2a**


jxp-5-195-noe
n-C6H13
H
H
NOE
O
O
I
Z-2a
n-C6H13
H
NO NOE
I
O
O
H
E-2a
ppm
ppm

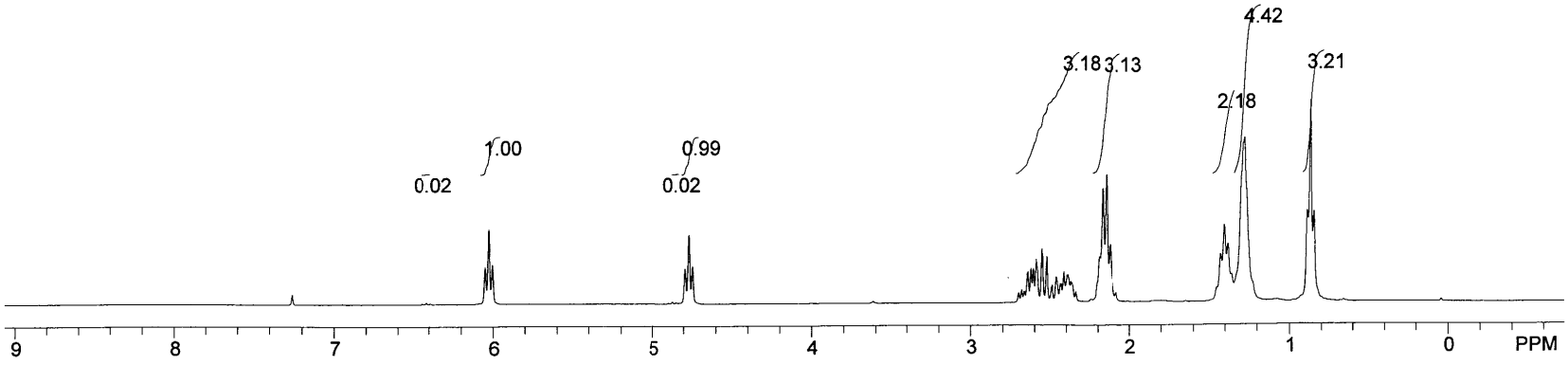

176.435
138.516
106.873
84.278
77.309
77.000
76.684
35.517
31.547
28.772
28.638
28.042
27.888
22.508
14.029
250
200
150
100
50
0
PPM
jxp-1-39-c
Z-2a
n-Hex
I
O
O

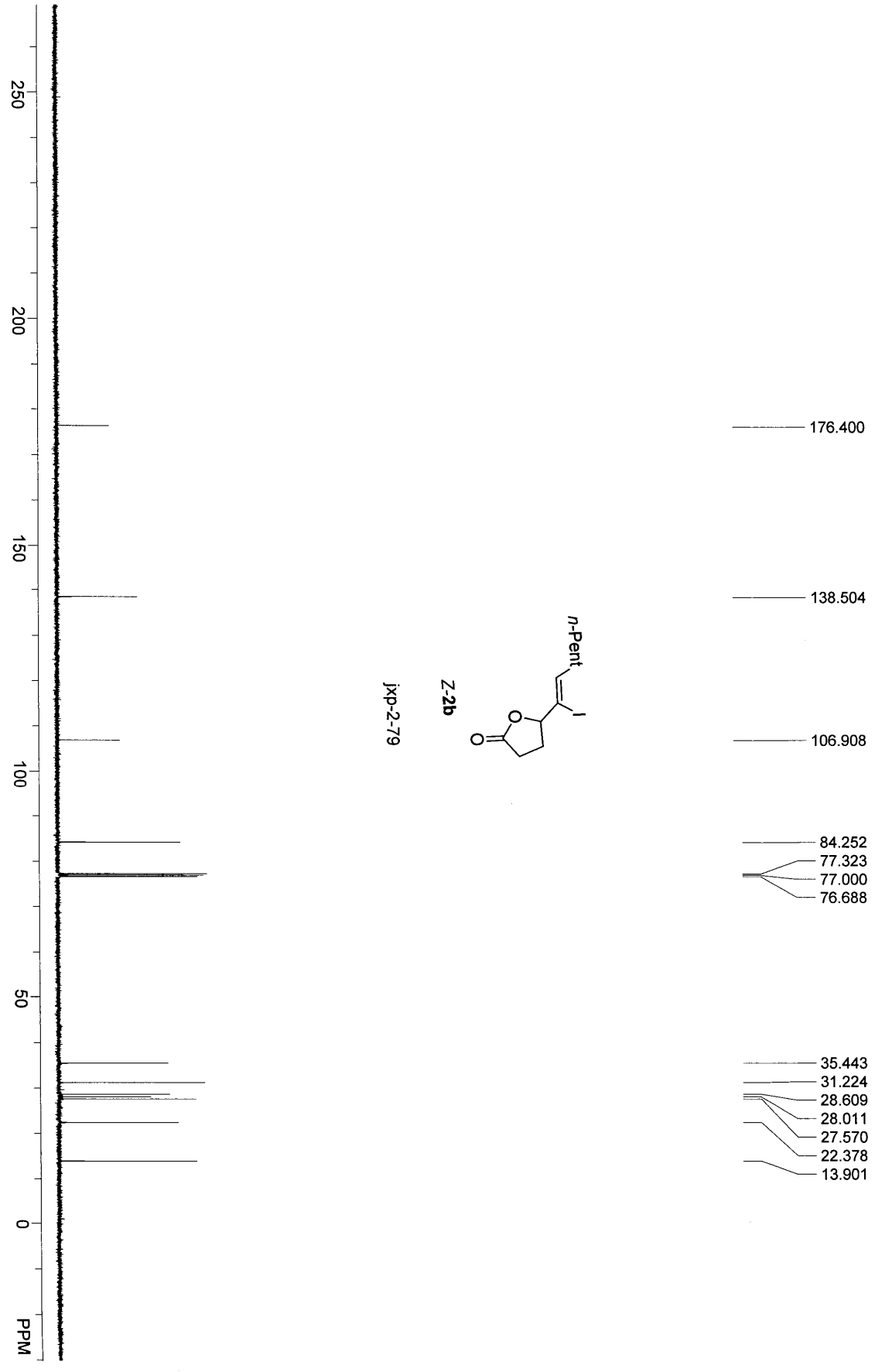

7.260
6.051
6.029
6.006
4.792
4.768
4.746
2.700
2.681
2.666
2.641
2.622
2.607
2.589
2.554
2.549
2.523
2.491
2.465
2.440
2.434
2.416
2.397
2.391
2.372
2.365
2.340
2.207
2.192
2.187
2.171
2.147
2.132
2.122
2.084
1.452
1.429
1.405
1.384
1.362
1.288
1.280
0.889
0.867
0.847

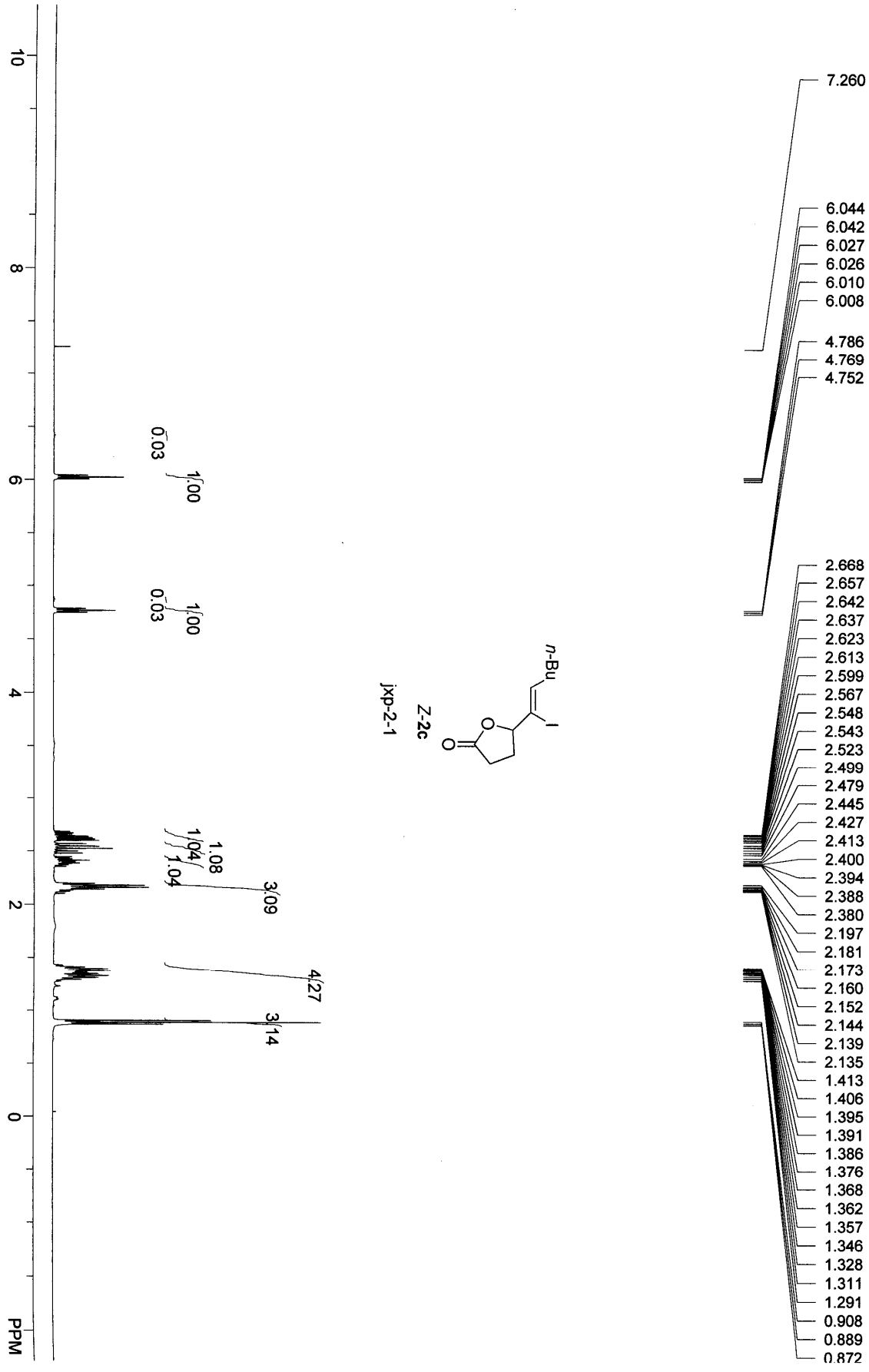

n-Pent
I
O
O

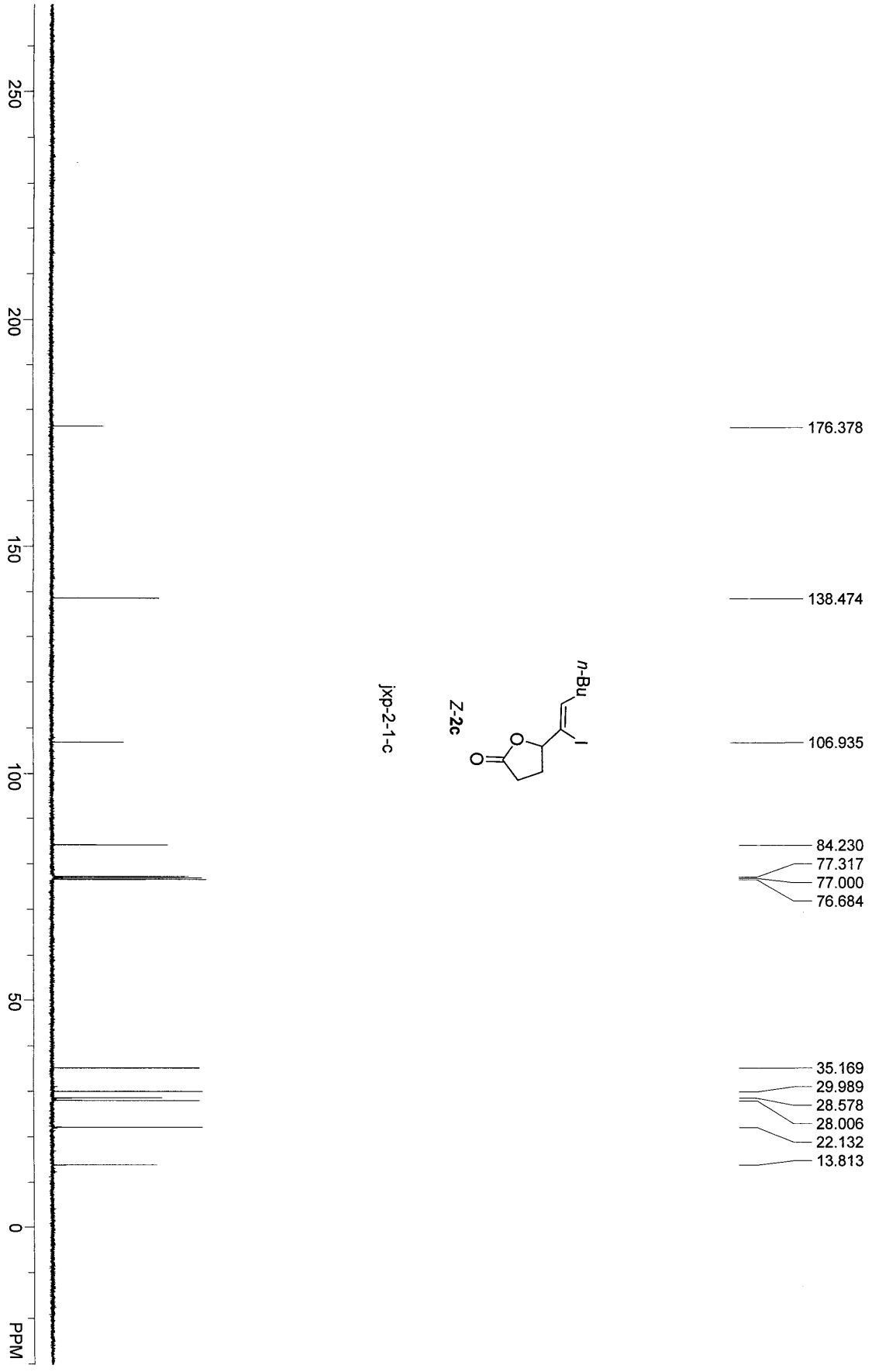
Z-**2b**

jxp-4-66


4.42
3.18
3.13
3.21
2.18
1.00
0.99
0.02
0.02
9
8
7
6
5
4
3
2
1
0
PPM


jxp-2-79
Z-2b
n-Pent
I
O
O
PPM
250
200
150
100
50
0
176.400
138.504
106.908
84.252
77.323
77.000
76.688
35.443
31.224
28.609
28.011
27.570
22.378
13.901


7.260
6.044
6.042
6.027
6.026
6.010
6.008
4.786
4.769
4.752
2.668
2.657
2.642
2.637
2.623
2.613
2.599
2.567
2.548
2.543
2.523
2.499
2.479
2.445
2.427
2.413
2.400
2.394
2.388
2.380
2.197
2.181
2.173
2.160
2.152
2.144
2.139
2.135
1.413
1.406
1.395
1.391
1.386
1.376
1.368
1.362
1.357
1.346
1.328
1.311
1.291
0.908
0.889
0.872
n-Bu
I
O
O
Z-2c
jxp-2-1
0.03
1.00
0.03
1.00
1.08
1.04
1.04
3.09
4.27
3.14
10
8
6
4
2
0
PPM


jxp-2-1-c
Z-2c
n-Bu
I
O
O
250
200
150
100
50
0
PPM
176.378
138.474
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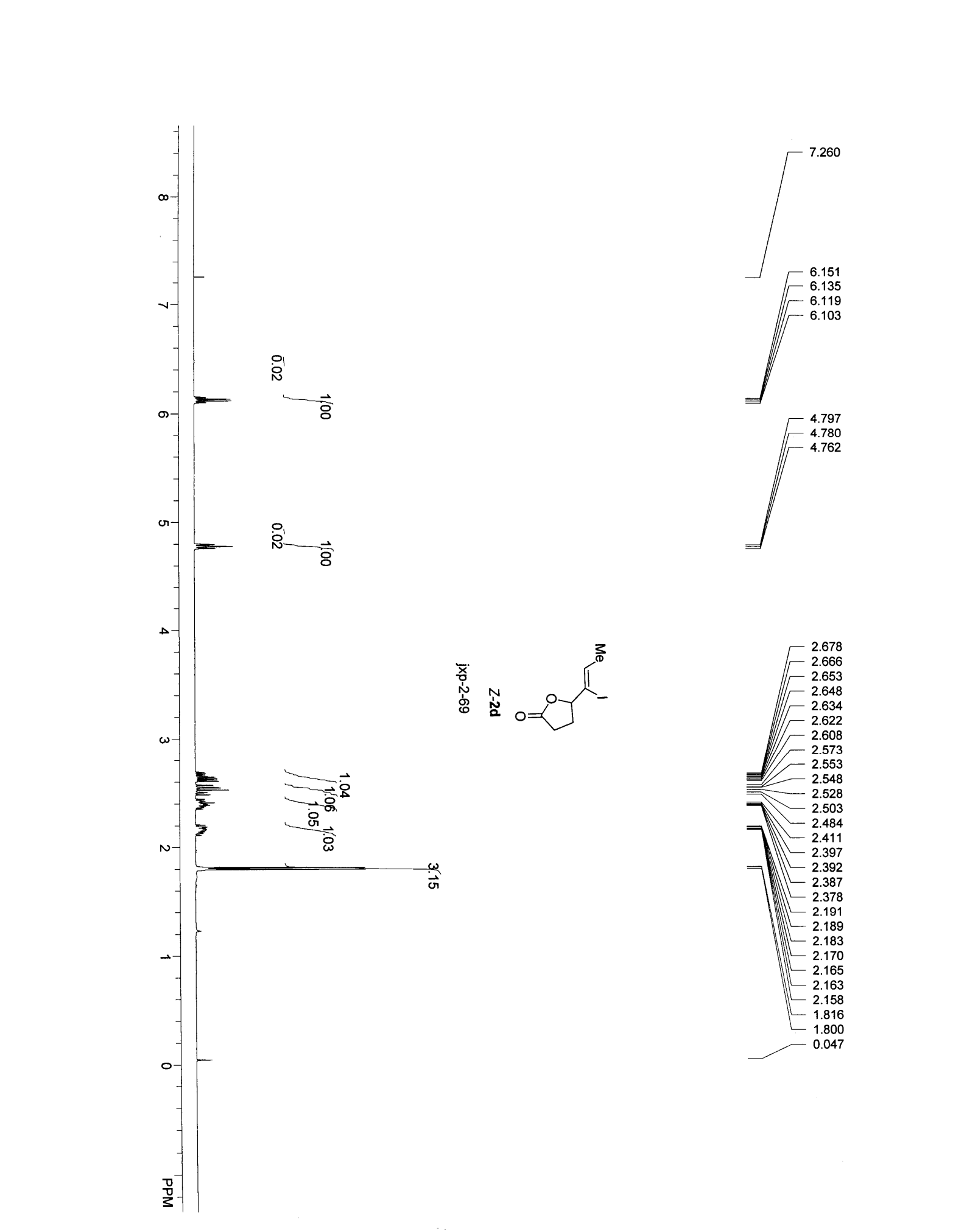
84.230
77.317
77.000
76.684
35.169
29.989
28.578
28.006
22.132
13.813


7.260
6.151
6.135
6.119
6.103
4.797
4.780
4.762
2.678
2.666
2.653
2.648
2.634
2.622
2.608
2.573
2.553
2.548
2.528
2.503
2.484
2.411
2.397
2.392
2.387
2.378
2.191
2.189
2.183
2.170
2.165
2.163
2.158
1.816
1.800
0.047
Me
I
O
O
Z-2d
jxp-2-69
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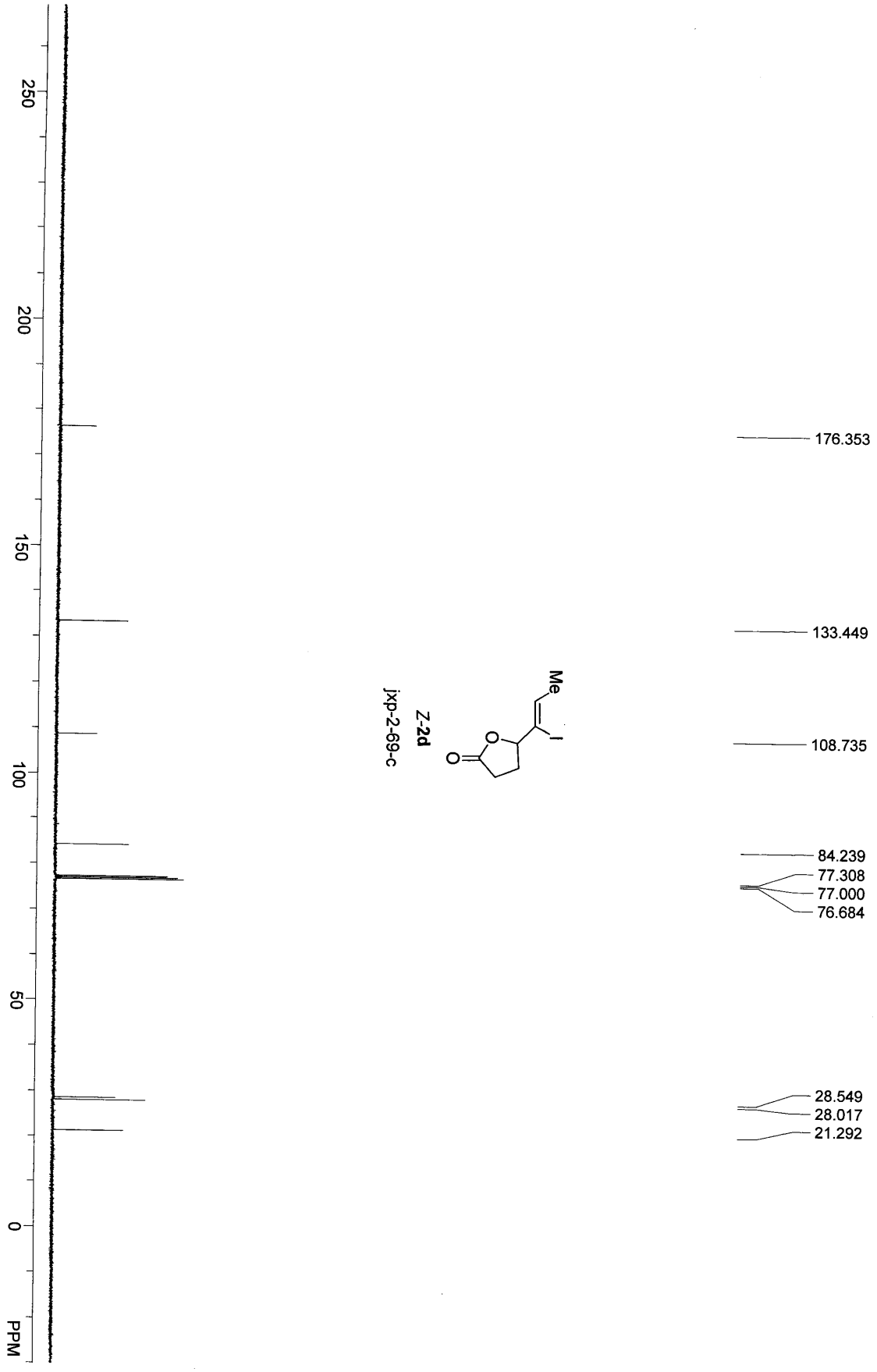
1.00
0.02
1.00
1.04
1.06
1.05
1.03
3.15
PPM


250
200
150
100
50
0
PPM
Z-2d
jxp-2-69-c
Me
I
O
O
176.353
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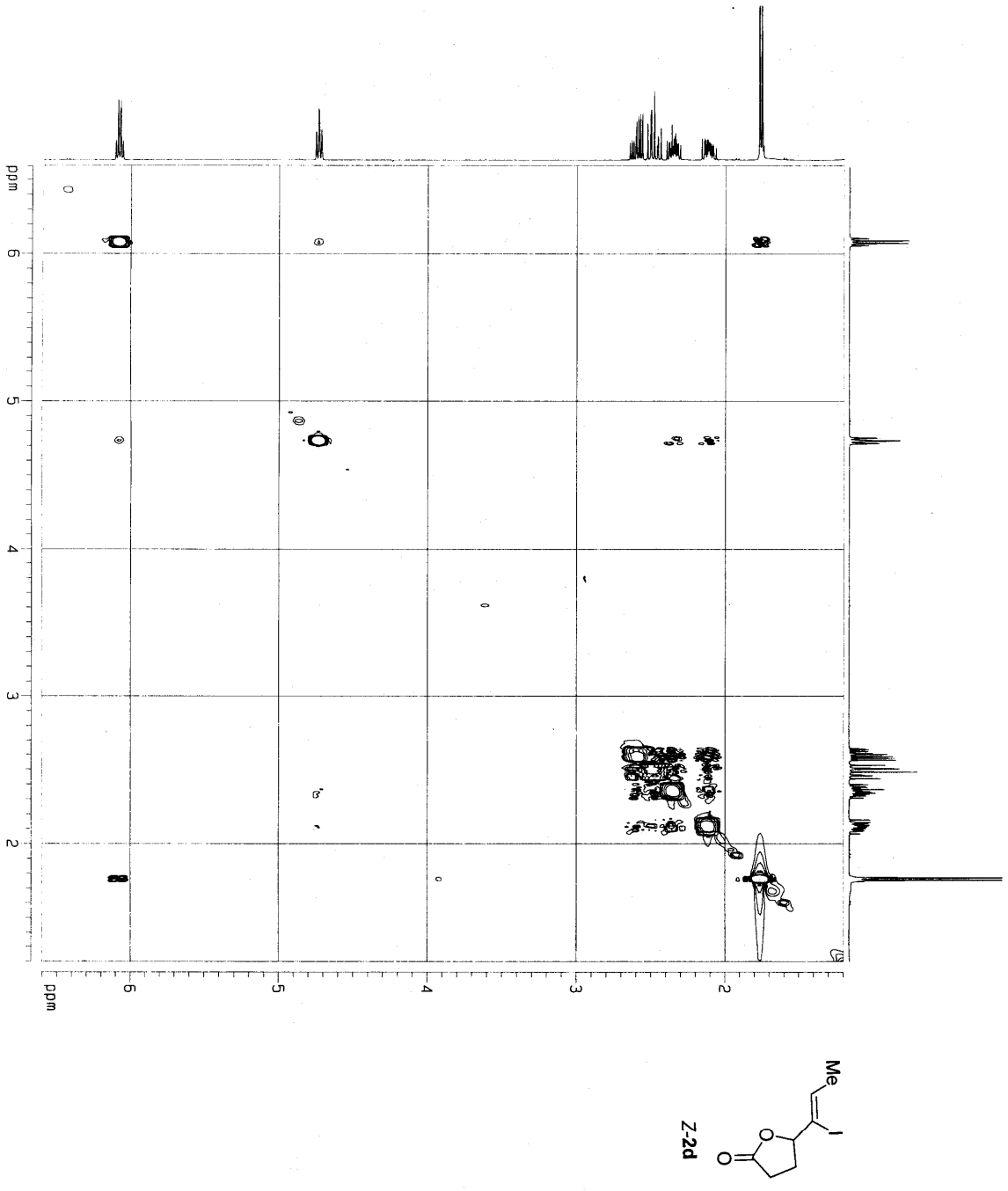
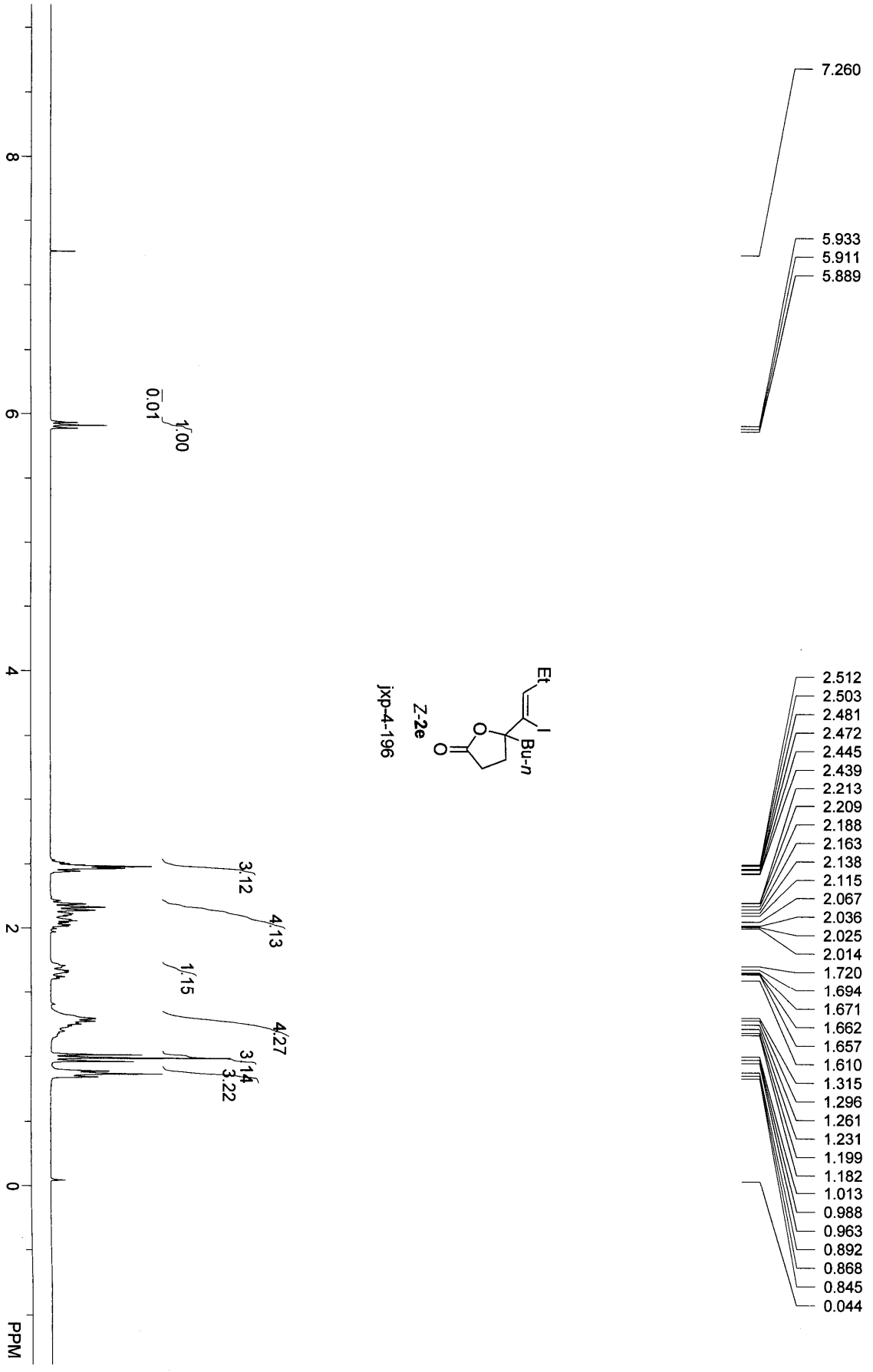
84.239
77.308
77.000
76.684
28.549
28.017
21.292

NOESY spectrum of *Z*-**2d**

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5.933
5.911
5.889
2.512
2.503
2.481
2.472
2.445
2.439
2.213
2.209
2.188
2.163
2.138
2.115
2.067
2.036
2.025
2.014
1.720
1.694
1.671
1.662
1.657
1.610
1.315
1.296
1.261
1.231
1.199
1.182
1.013
0.988
0.963
0.892
0.868
0.845
0.044
Et
Bu-n
O
O
O
Z-2e
jxp-4-196
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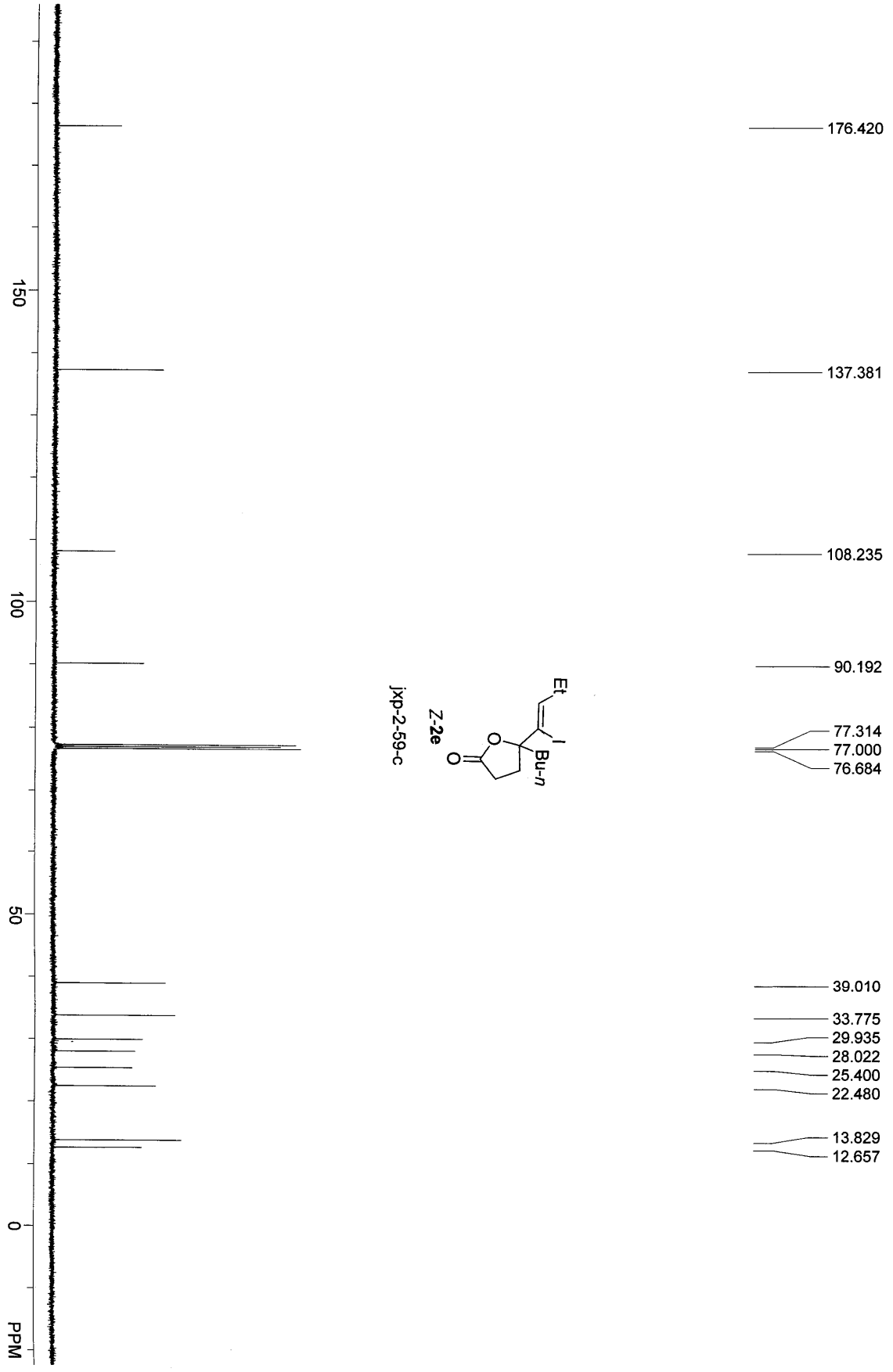
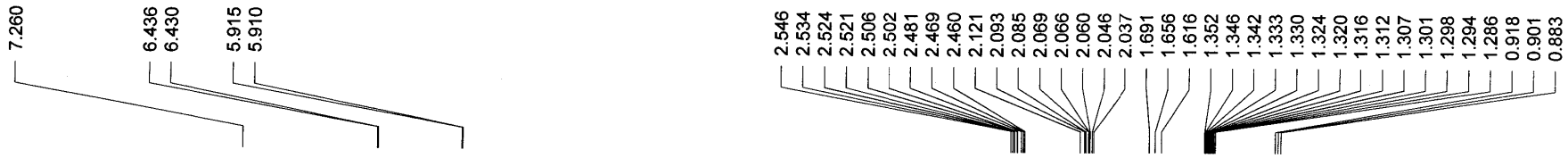
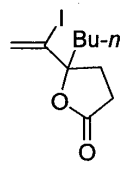
1.00
3.12
4.13
1.15
4.27
3.14
3.22
8
6
4
2
0
PPM

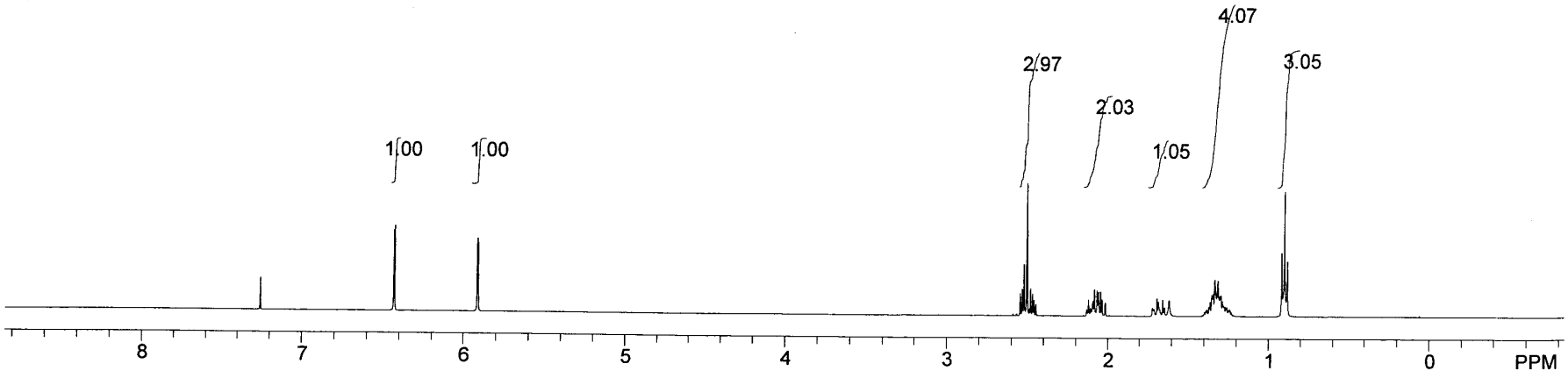

176.420
137.381
108.235
90.192
77.314
77.000
76.684
39.010
33.775
29.935
28.022
25.400
22.480
13.829
12.657
150
100
50
0
PPM
jxp-2-59-c
Z-2e
Et
I
Bu-n
O
O

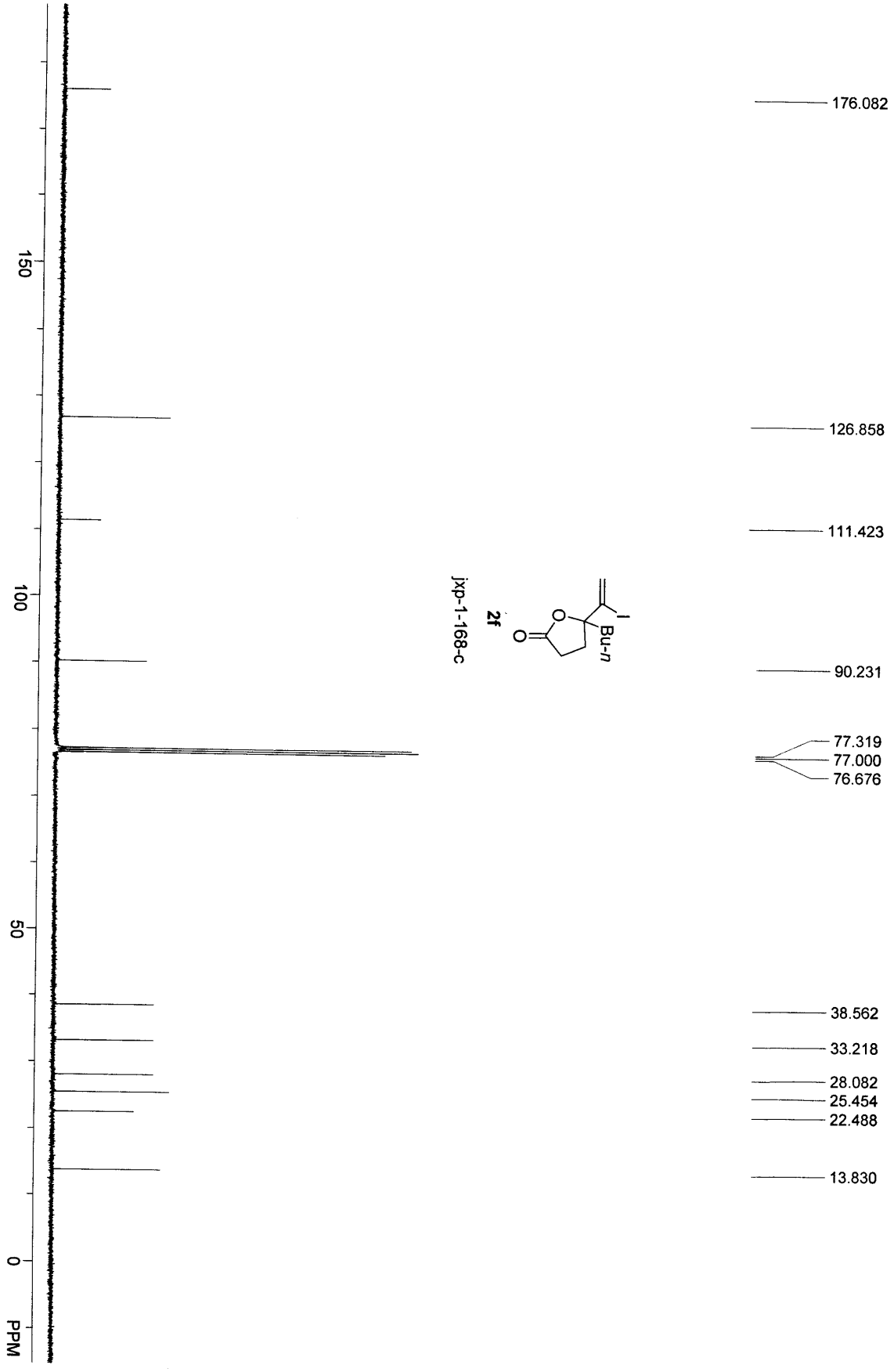

7.260
6.436
6.430
5.915
5.910
2.546
2.534
2.524
2.521
2.506
2.502
2.481
2.469
2.460
2.121
2.093
2.085
2.069
2.066
2.060
2.046
2.037
1.691
1.656
1.616
1.352
1.346
1.342
1.333
1.330
1.324
1.320
1.316
1.312
1.307
1.301
1.298
1.294
1.286
0.918
0.901
0.883

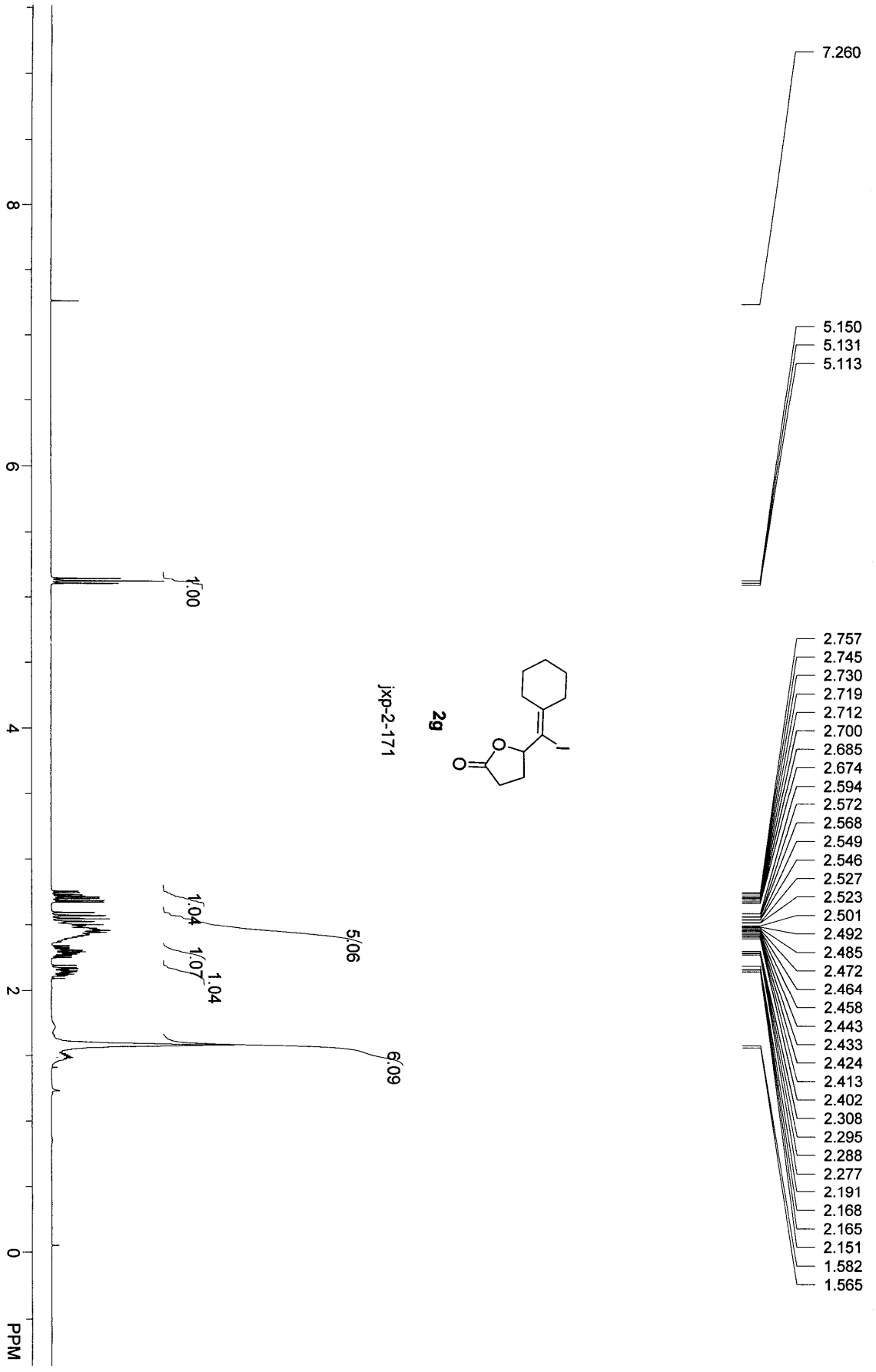

I
Bu-n
O
O

2f

jxp-1-168


1.00
1.00
2.97
2.03
1.05
4.07
3.05
8
7
6
5
4
3
2
1
0
PPM


176.082
126.858
111.423
90.231
77.319
77.000
76.676
38.562
33.218
28.082
25.454
22.488
13.830
150
100
50
0
PPM
jxp-1-168-c
2f
Bu-n


7.260
5.150
5.131
5.113
2.757
2.745
2.730
2.719
2.712
2.700
2.685
2.674
2.594
2.572
2.568
2.549
2.546
2.527
2.523
2.501
2.492
2.485
2.472
2.464
2.458
2.443
2.433
2.424
2.413
2.402
2.308
2.295
2.288
2.277
2.191
2.168
2.165
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1.04
1.07
1.04
5.06
6.09
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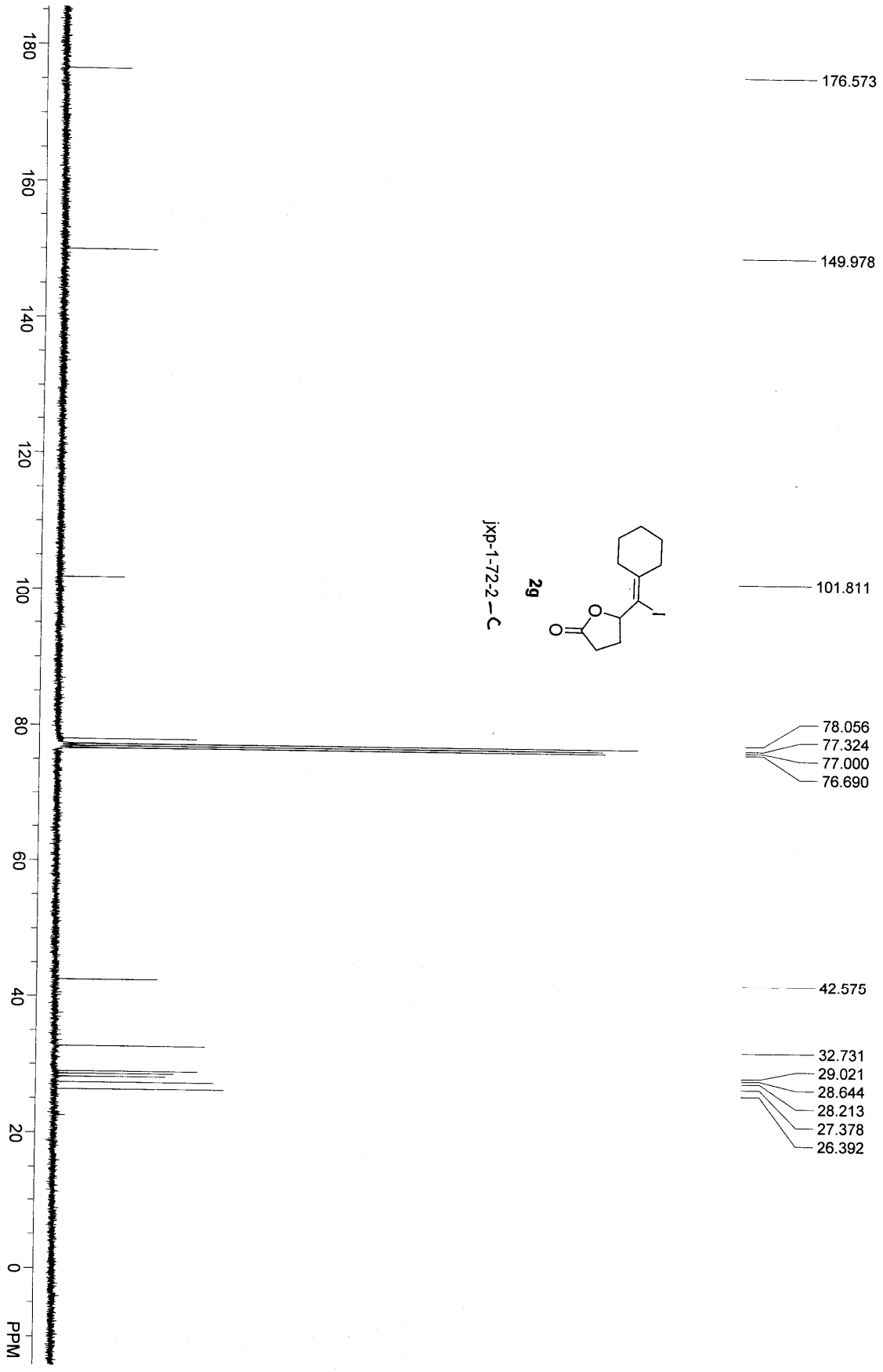
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26.392
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I
O
O
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140
120
100
80
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20
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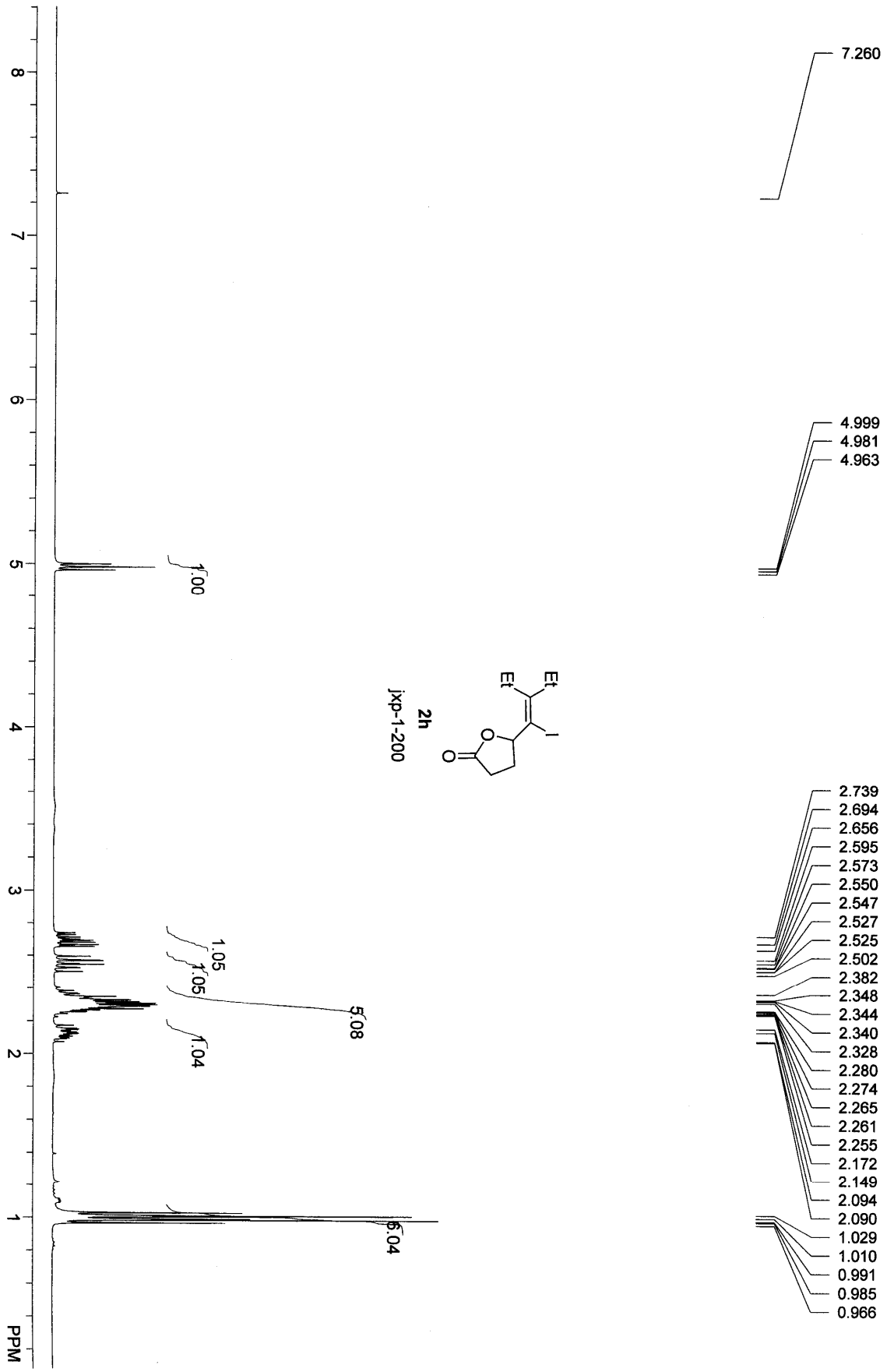
PPM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2.739
2.694
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2.547
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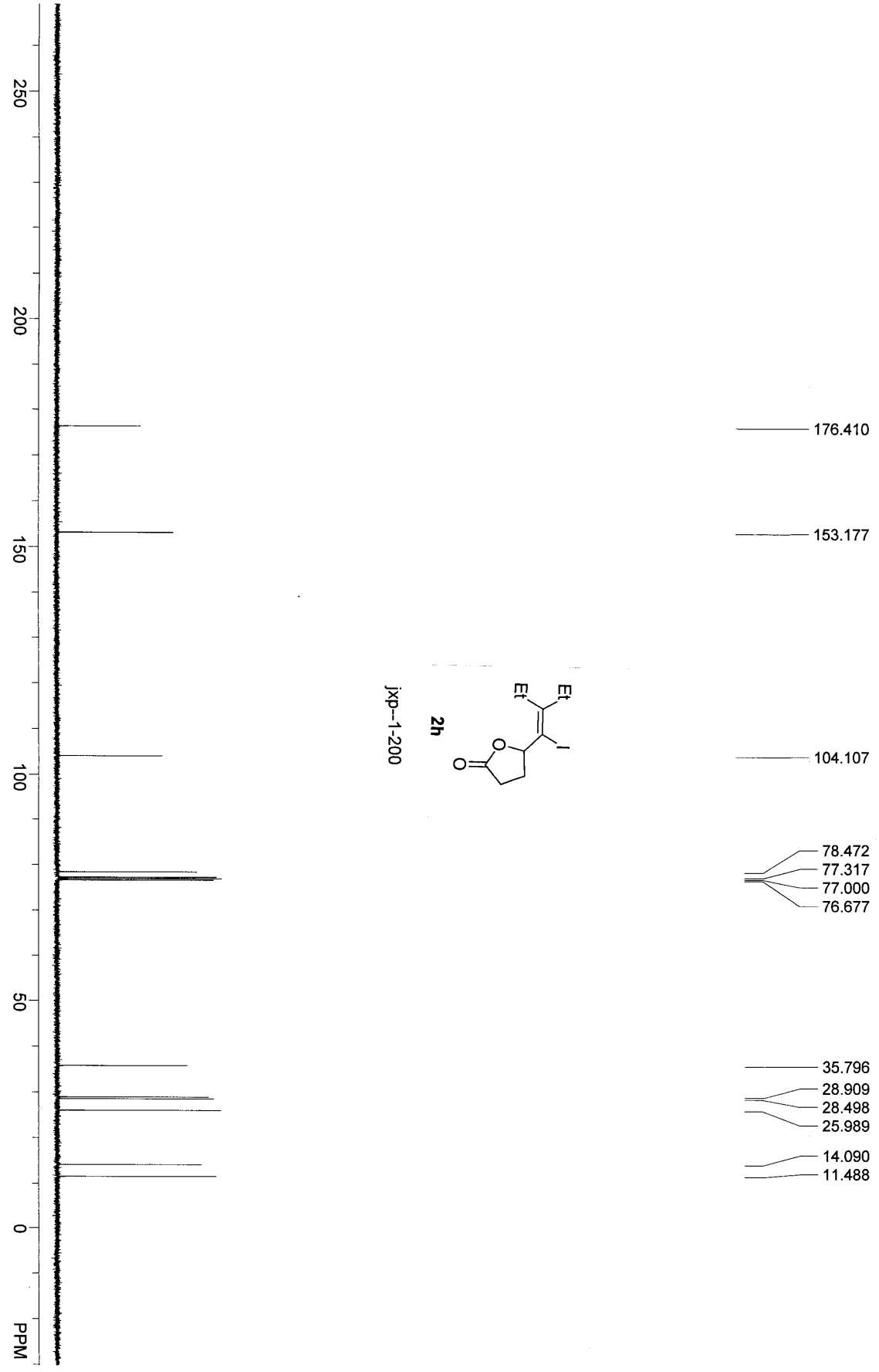
2.525
2.502
2.382
2.348
2.344
2.340
2.328
2.280
2.274
2.265
2.261
2.255
2.172
2.149
2.094
2.090
1.029
1.010
0.991
0.985
0.966
2h
jxp-1-200
Et
Et
I
O
O
1.00
1.05
1.05
5.08
1.04
6.04
PPM
8
7
6
5
4
3
2
1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200
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50
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PPM
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2h
Et
Et
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O
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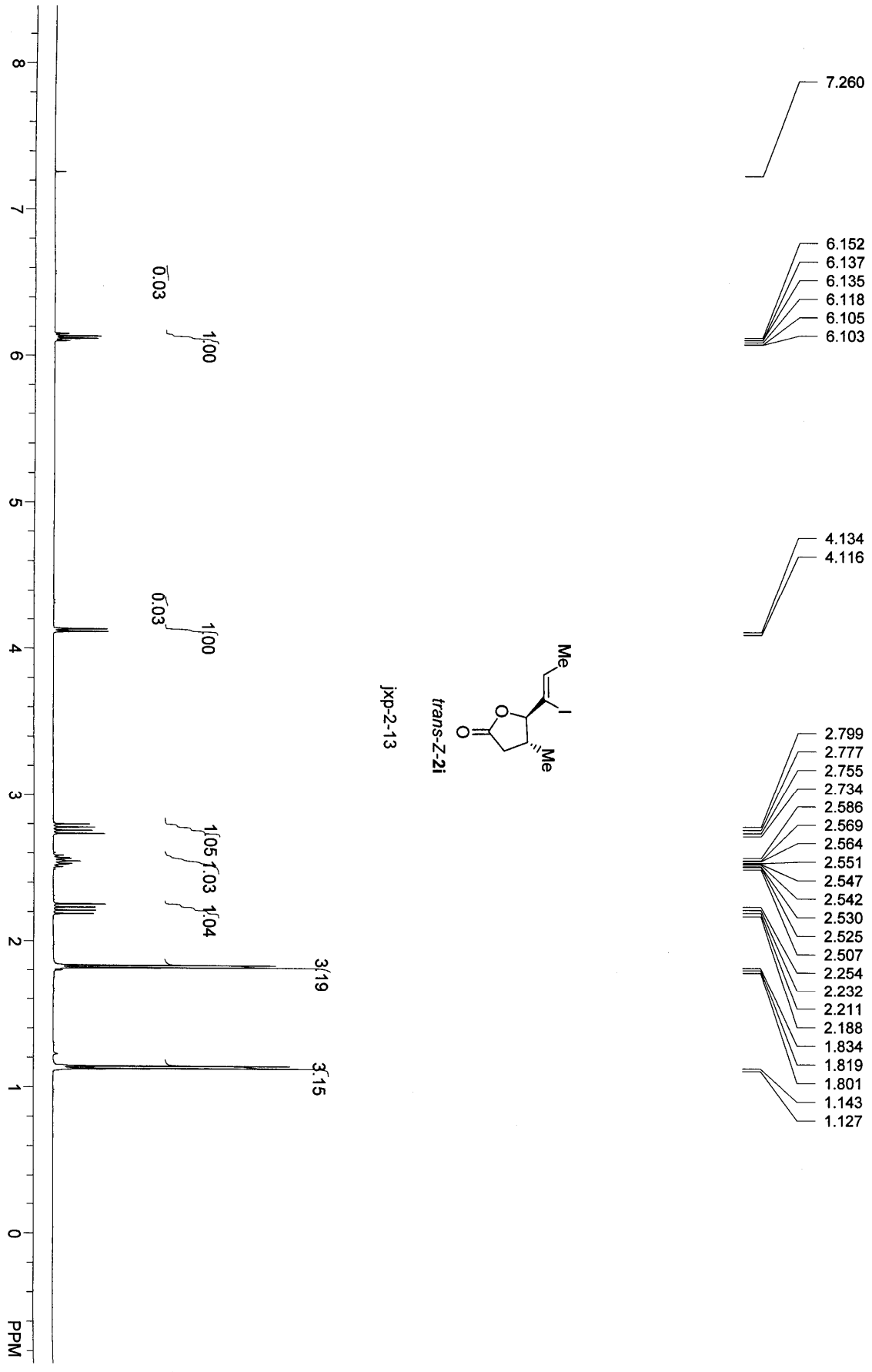
11.488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6.105
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4.134
4.116
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2.734
2.586
2.569
2.564
2.551
2.547
2.542
2.530
2.525
2.507
2.254
2.232
2.211
2.188
1.834
1.819
1.801
1.143
1.127
Me
O
O
Me
trans-Z-2i
jxp-2-13
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1.00
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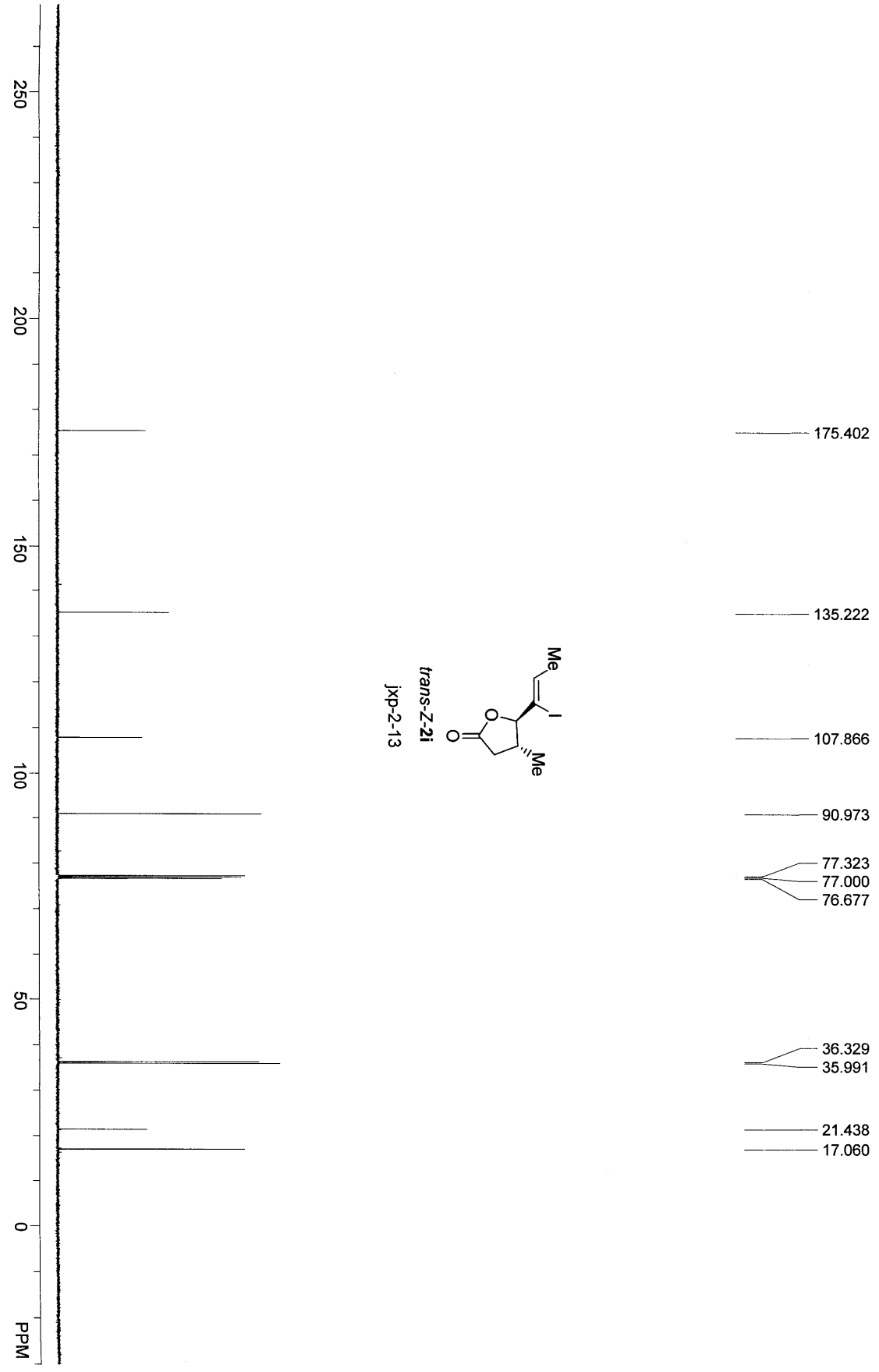
1.00
1.05
1.03
1.04
3.19
3.15
PPM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200
150
100
50
0
PPM
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90.973
77.323
77.000
76.677
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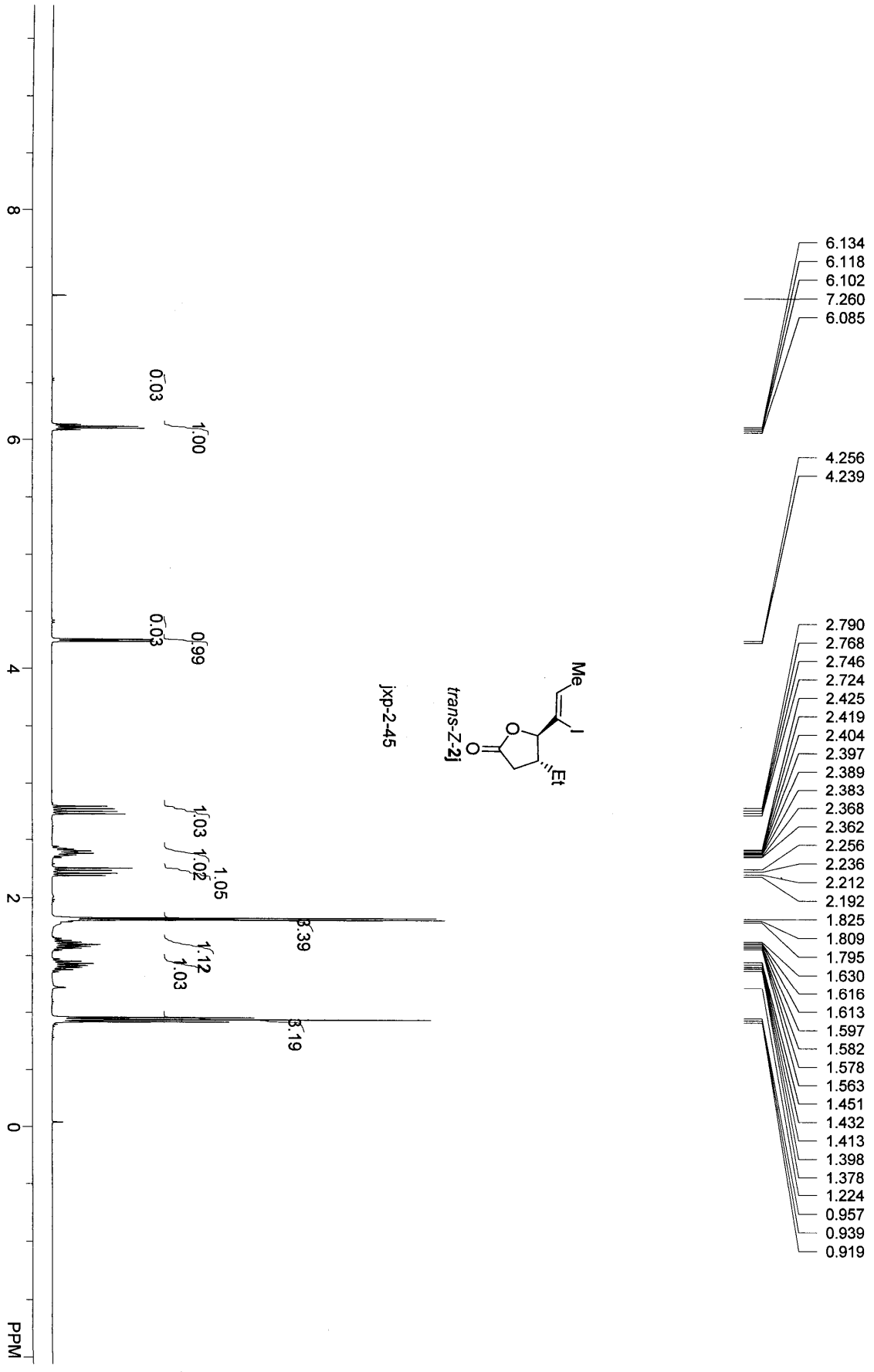
35.991
21.438
17.060
trans-Z-2i
jxp-2-13
Me
I
O
O
Me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2.419
2.404
2.397
2.389
2.383
2.368
2.362
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2.212
2.192
1.825
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1.795
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1.597
1.582
1.578
1.563
1.451
1.432
1.413
1.398
1.378
1.224
0.957
0.939
0.919
Me
I
O
O
Et
trans-Z-2j
jxp-2-45
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1.00
0.03
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1.02
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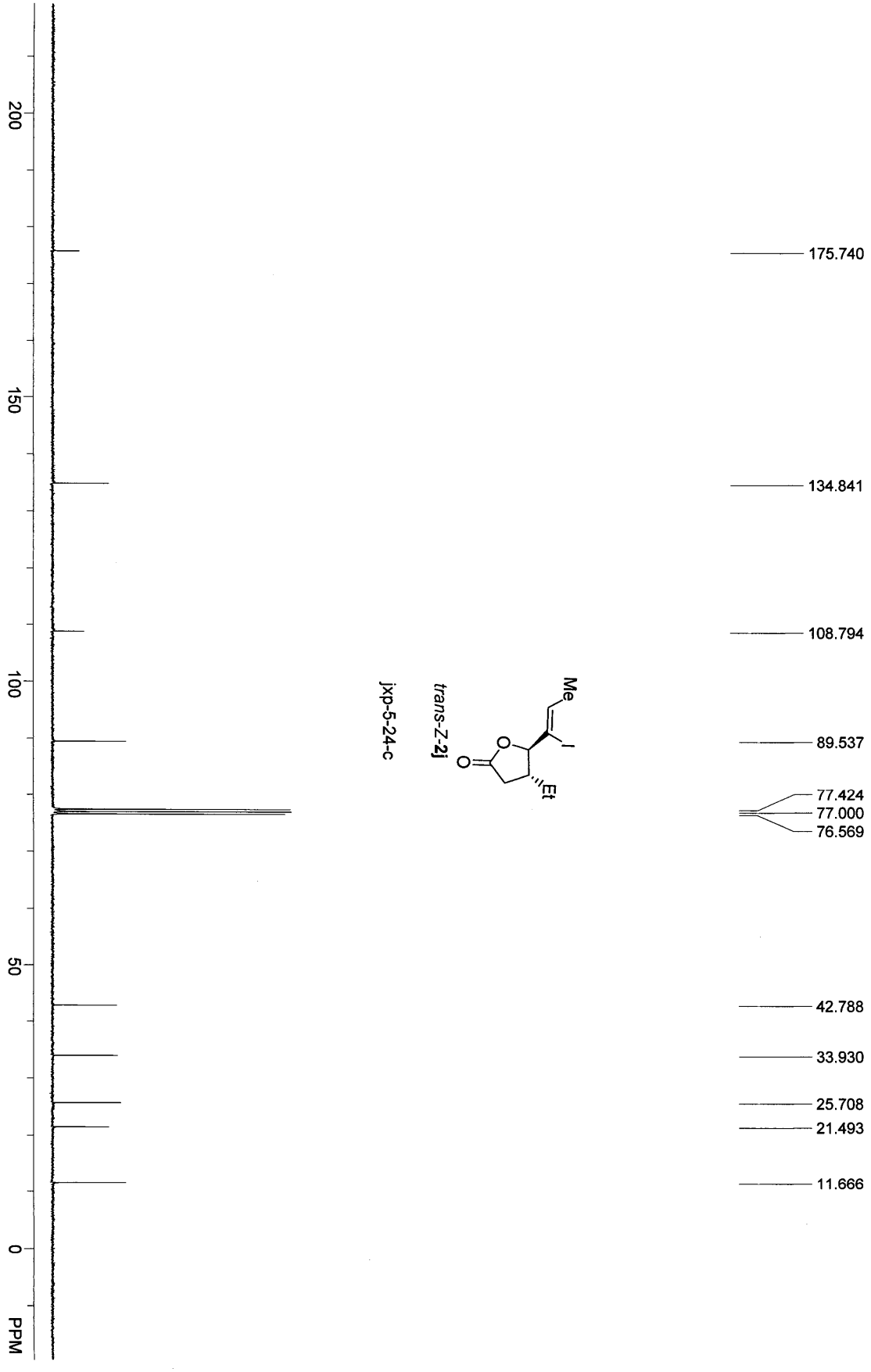
1.03
3.19
8
6
4
2
0
PPM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150
100
50
0
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89.537
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77.000
76.569
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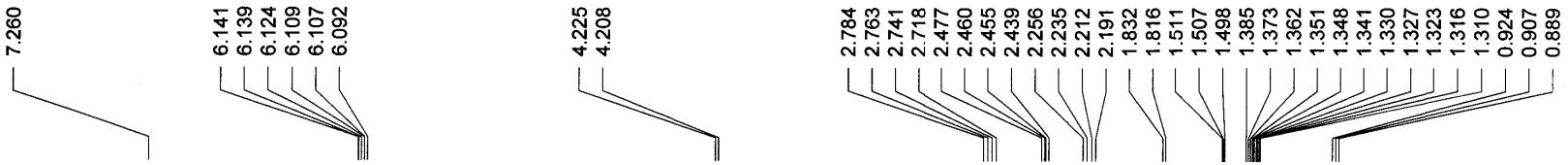
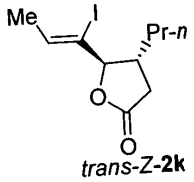
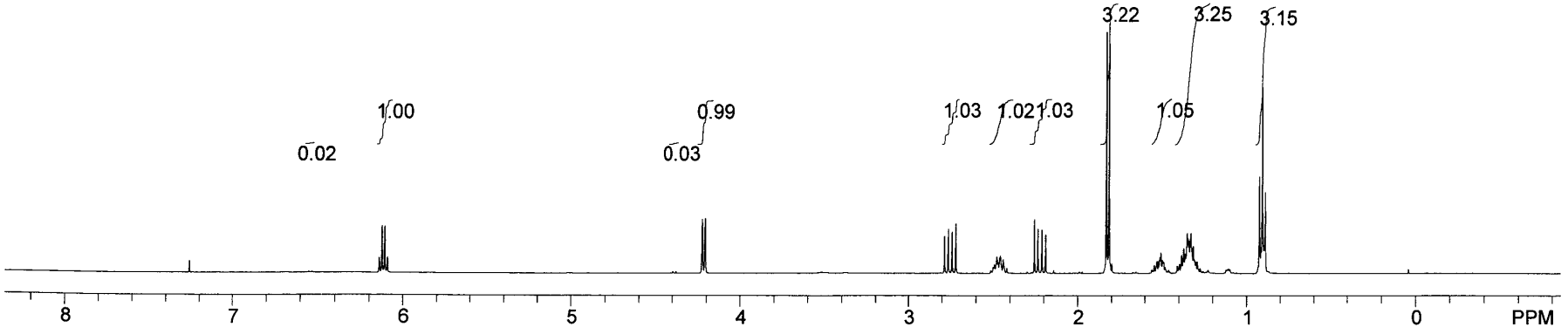
25.708
21.493
11.666
jxp-5-24-c
trans-Z-2j
Me
I
Et
O
O

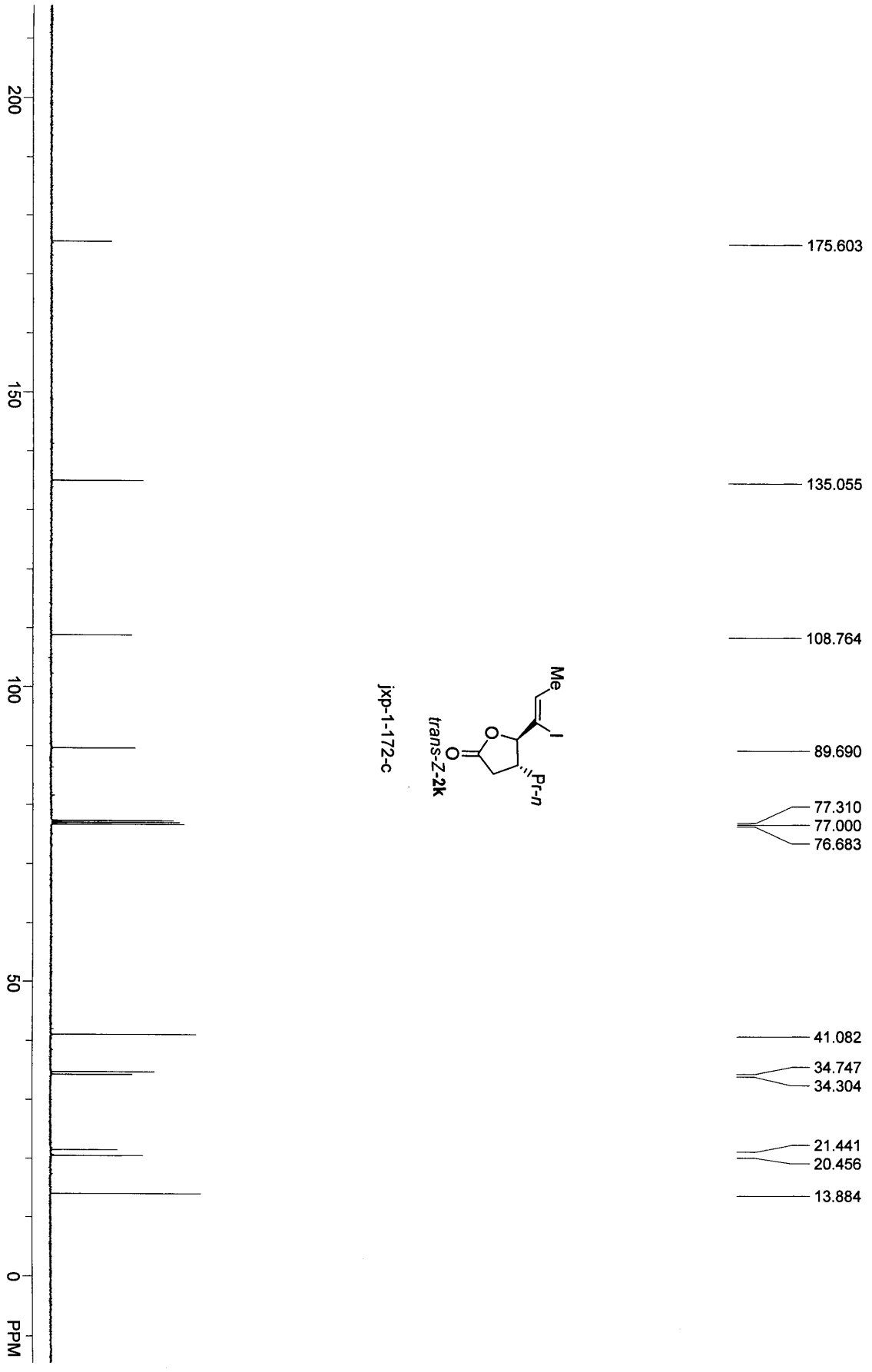




trans-Z-**2k**

jxp-1--172

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100
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0
PPM
jxp-1-172-c
trans-Z-2k
Me
I
Pr-n
O
O
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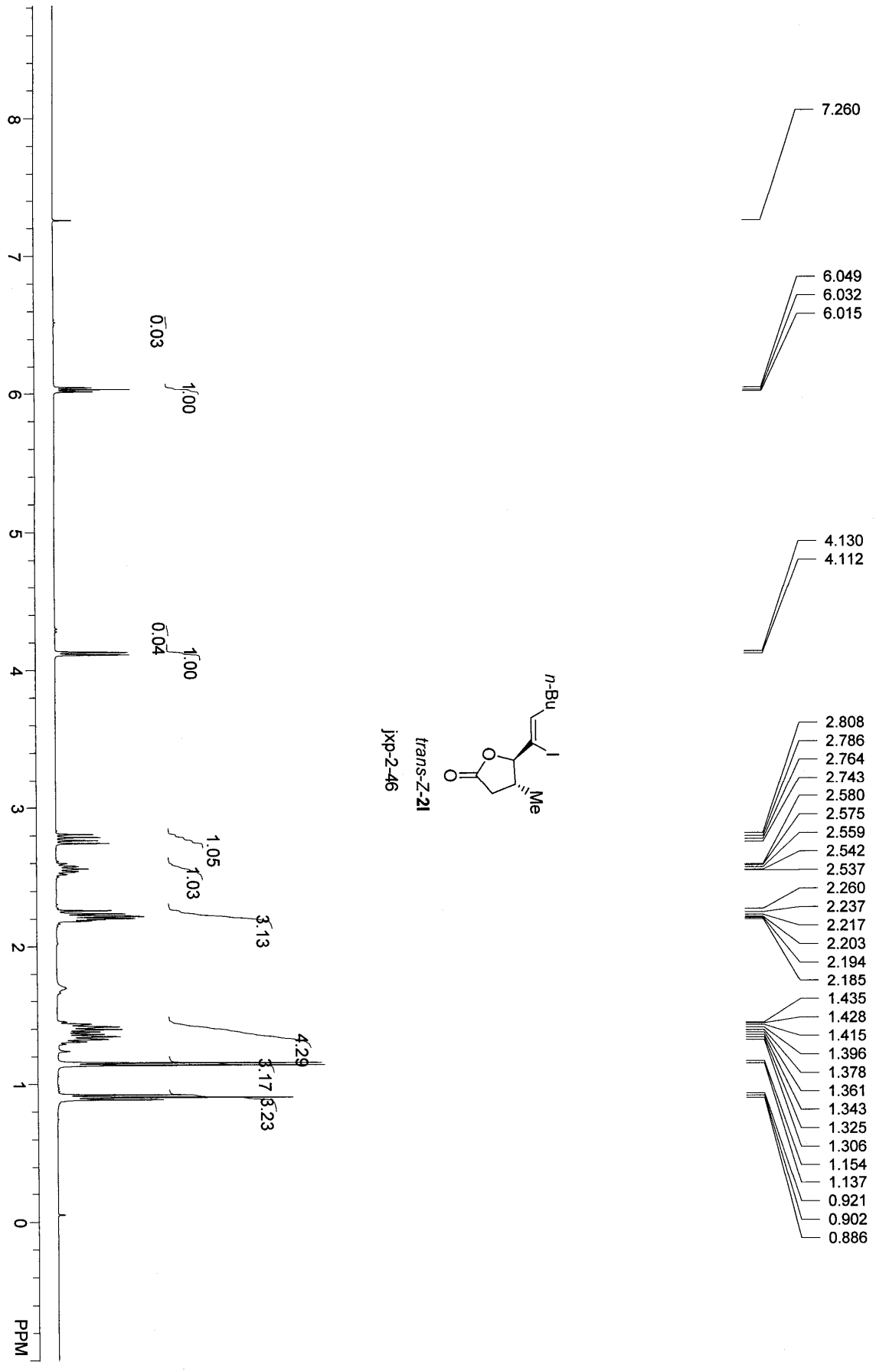
89.690
77.310
77.000
76.683
41.082
34.747
34.304
21.441
20.456
13.884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6.015
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4.112
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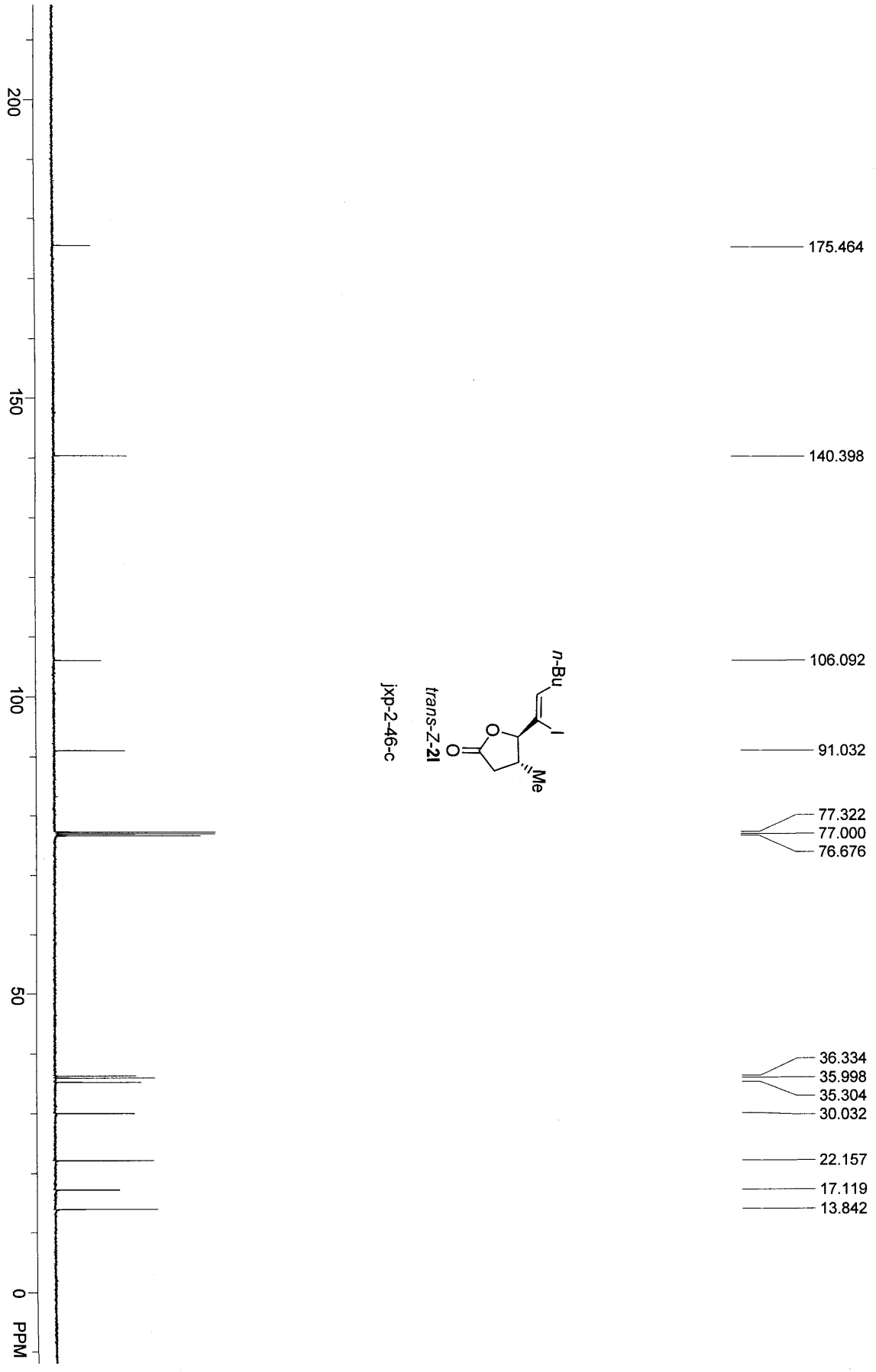
2.786
2.764
2.743
2.580
2.575
2.559
2.542
2.537
2.260
2.237
2.217
2.203
2.194
2.185
1.435
1.428
1.415
1.396
1.378
1.361
1.343
1.325
1.306
1.154
1.137
0.921
0.902
0.886
0.03
1.00
0.04
1.00
1.05
1.03
3.13
4.29
3.17
3.23
PPM
n-Bu
Me
trans-Z-2l
jxp-2-46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trans-Z-2l
n-Bu
I
O
O
Me
200
150
100
50
0
PPM
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140.398
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91.032
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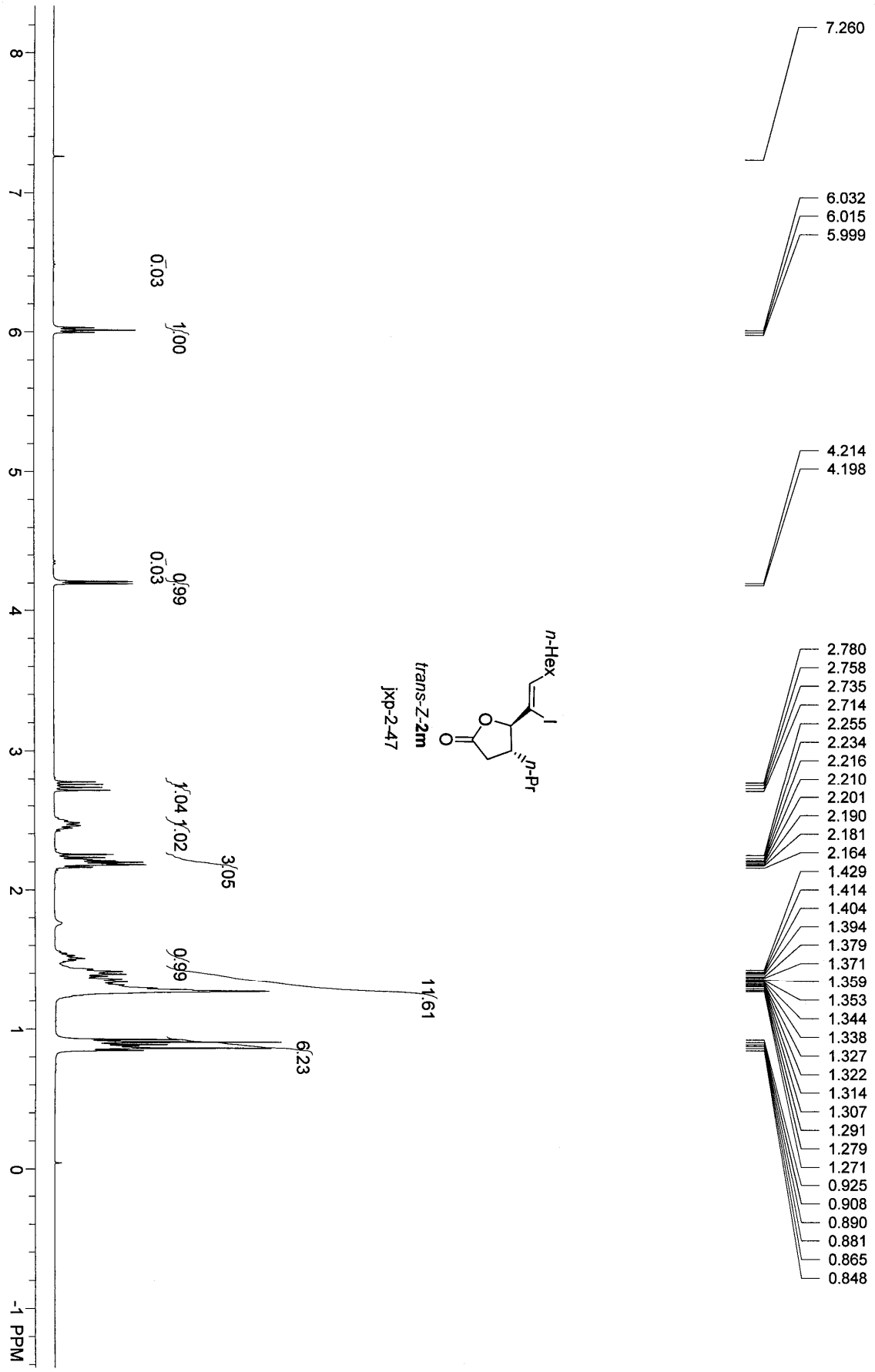
77.000
76.676
36.334
35.998
35.304
30.032
22.157
17.119
13.842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2.714
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2.234
2.216
2.210
2.201
2.190
2.181
2.164
1.429
1.414
1.404
1.394
1.379
1.371
1.359
1.353
1.344
1.338
1.327
1.322
1.314
1.307
1.291
1.279
1.271
0.925
0.908
0.890
0.881
0.865
0.848
n-Hex
n-Pr
trans-Z-2m
jxp-2-47
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1.00
0.03
0.99
1.04
1.02
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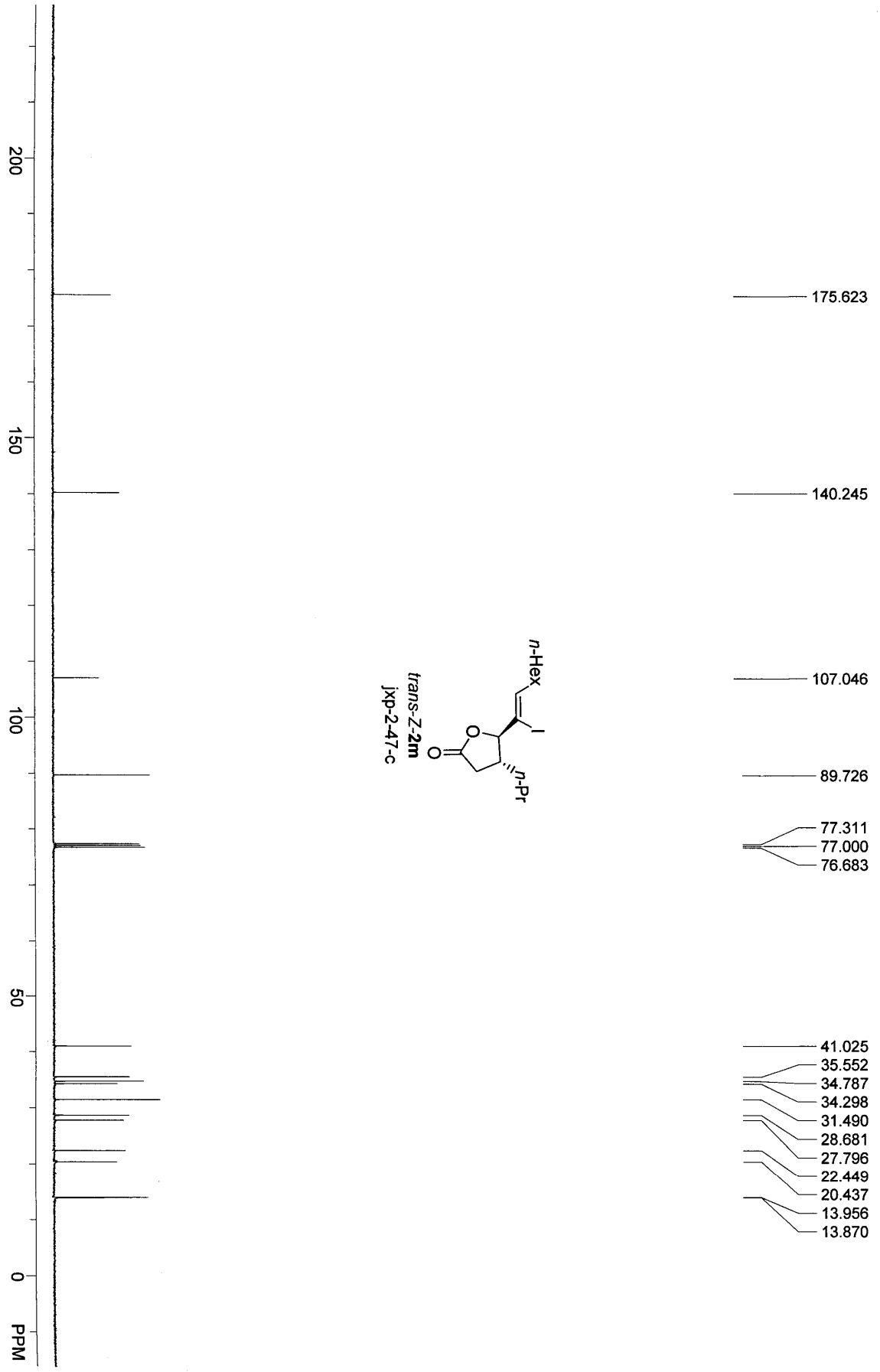
0.99
11.61
6.23
8
7
6
5
4
3
2
1
0
-1 PPM


200
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100
50
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PPM
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I
O
O
n-Pr
trans-Z-2m
jxp-2-47-c
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140.245
107.046
89.726
77.311
77.000
76.683
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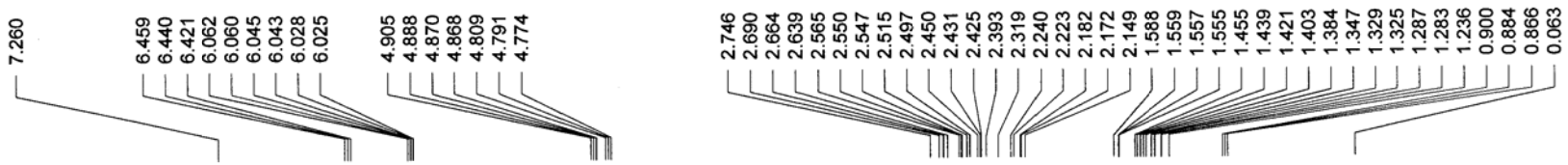
31.490
28.681
27.796
22.449
20.437
13.956
13.870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6.025
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4.870
4.868
4.809
4.791
4.774
2.746
2.690
2.664
2.639
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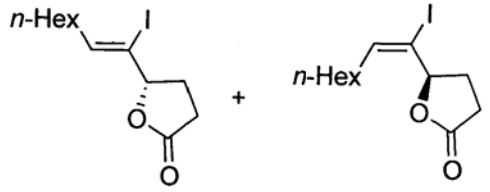
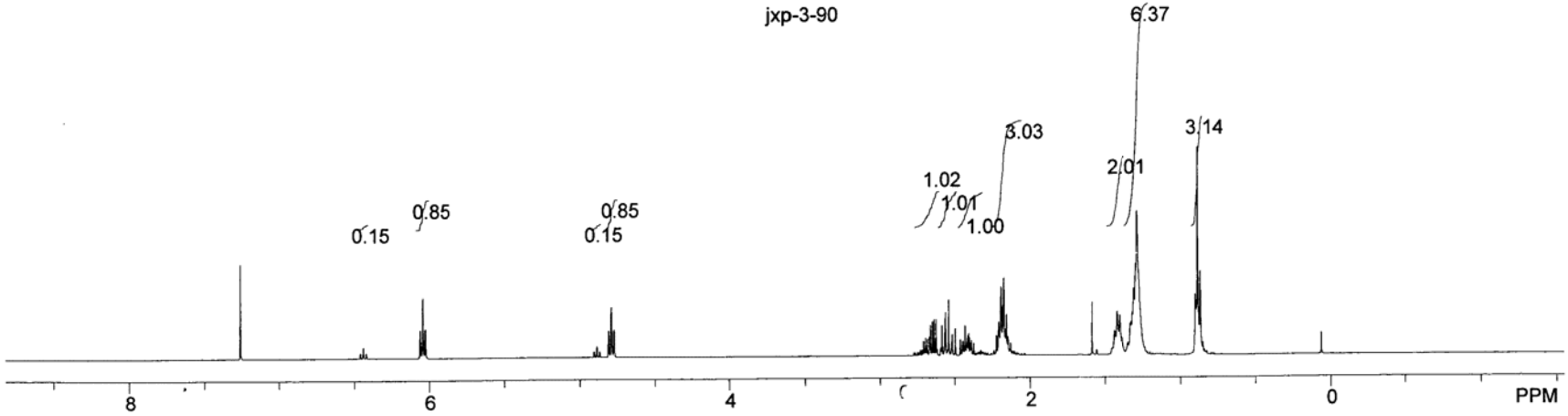
2.550
2.547
2.515
2.497
2.450
2.431
2.425
2.393
2.319
2.240
2.223
2.182
2.172
2.149
1.588
1.559
1.557
1.555
1.455
1.439
1.421
1.403
1.384
1.347
1.329
1.325
1.287
1.283
1.236
0.900
0.884
0.866
0.063


n-Hex
I
O
O
+
n-Hex
I
O
O

(*S*)-*Z*-**2a** (*R*)-*E*-**2a**


jxp-3-90
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3.03
3.14
2.01
1.02
1.01
1.00
0.85
0.15
0.85
0.15
8
6
4
2
0
PPM

The HPLC spectrum of the mixture of (*S*)-*Z*-**2a** and (*R*)-*E*-**2a**

Data File D:\HPCHEM\1\DATA\JXP\JXP00167.D Sample Name: jxp-3-9

n-Hexane:i-PrOH = 90/10, n=254 nm, 0.5 ml/min, OJ-H

```
==========================================================================
Injection Date  : 10/5/2007 8:19:15 PM
Sample Name     : jxp-3-90                        Location : Vial 1
Acq. Operator   : jxp
Acq. Method     : D:\HPCHEM\1\METHODS\SY-ESTER.M
Last changed    : 10/5/2007 7:22:26 PM by jxp
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\SY-ESTER.M
Last changed    : 9/16/2007 10:59:57 AM by sy
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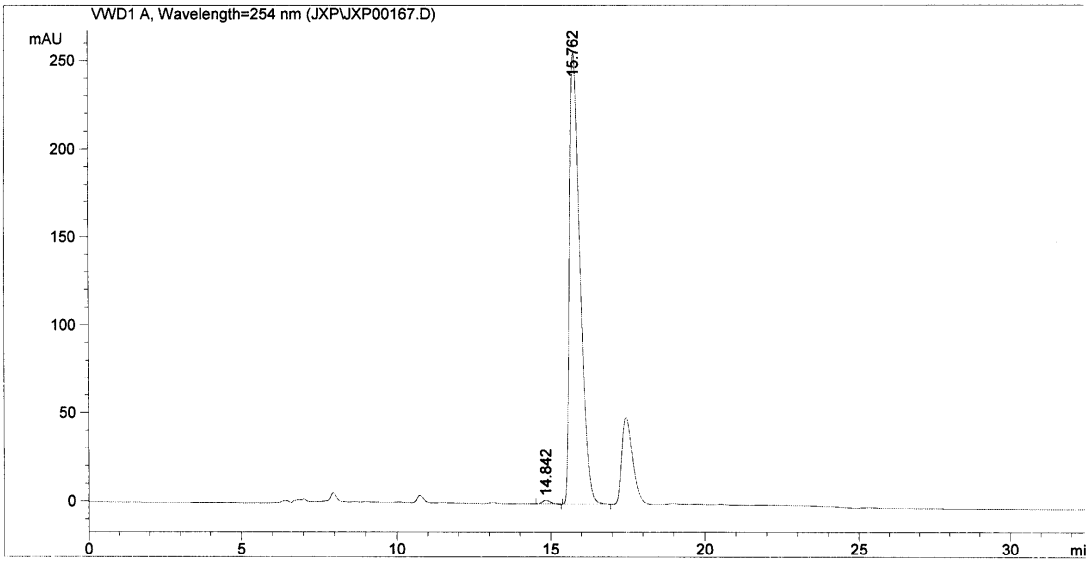


```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.842 PP    0.2770   36.61198    2.04789   0.5986
   2  15.762 BB    0.3689 6079.19287  255.84001  99.4014

Totals :                  6115.80486  257.88790

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

Instrument 1 10/6/2007 9:11:31 AM jxp Page 1 of 1

The HPLC spectrum of racemic *Z*-**2a**

ata File D:\HPCHEM\1\DATA\JXP\JXP00170.D Sample Name: jxp-C6-w

n-Hexane:i-PrOH = 90/10, n=254 nm, 0.5 ml/min, OJ-H

```
==========================================================================
Injection Date  : 10/5/2007 9:53:35 PM
Sample Name     : jxp-C6-wx                        Location : Vial 1
Acq. Operator   : jxp
Acq. Method     : D:\HPCHEM\1\METHODS\SY-ESTER.M
Last changed    : 10/5/2007 7:22:26 PM by jxp
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\SY-ESTER.M
Last changed    : 9/16/2007 10:59:57 AM by sy
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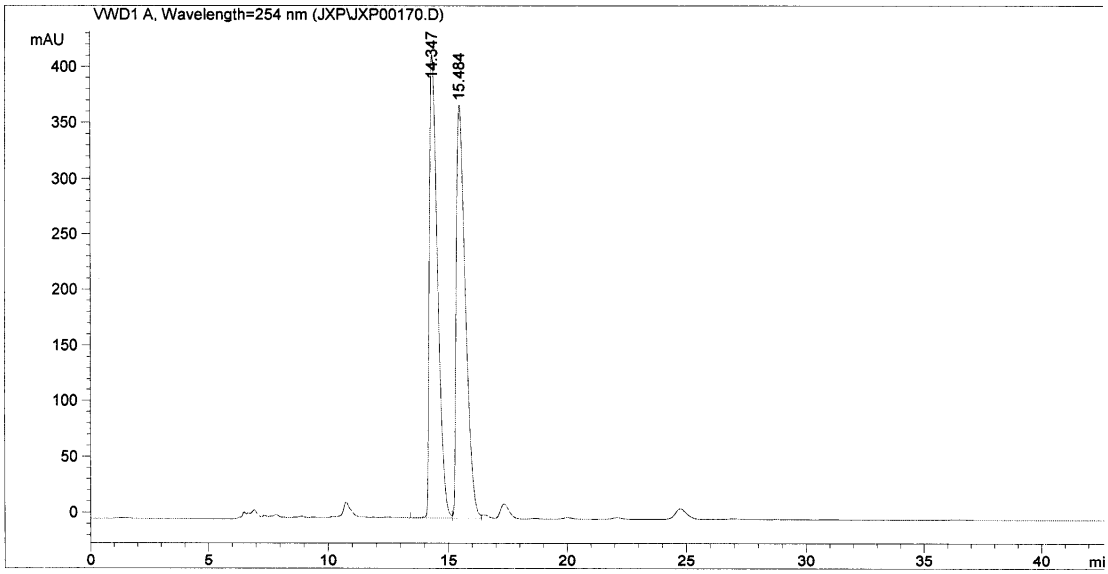


```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.347 VV    0.3676 9887.61328  415.96988  50.0977
   2  15.484 VV    0.4073 9849.04980  370.93872  49.9023

Totals :                  1.97367e4   786.90860

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
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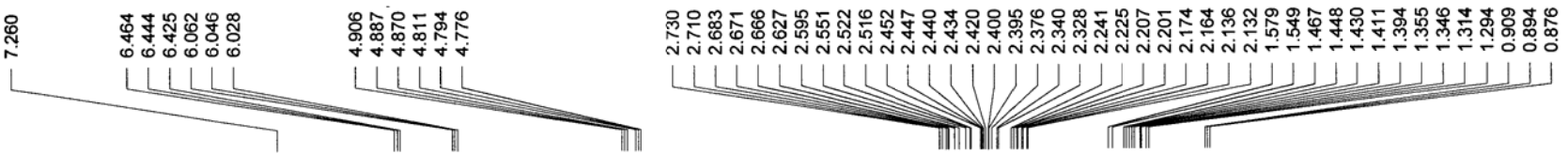
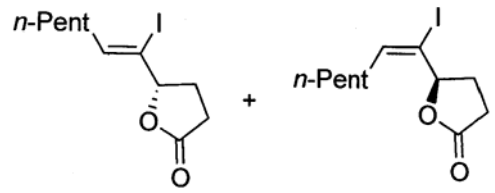
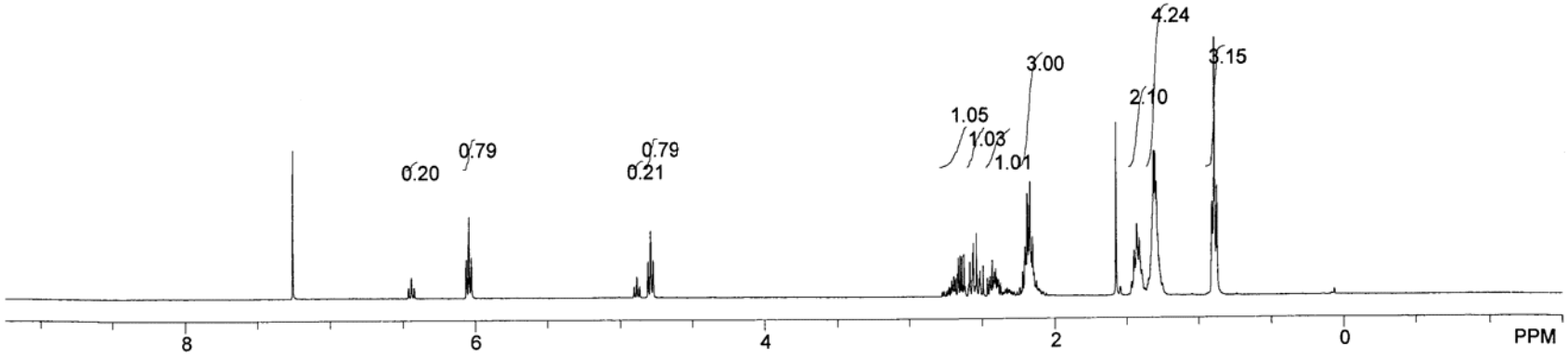




(*S*)-*Z*-**2b** (*R*)-*E*-**2b**

jxp-4-2

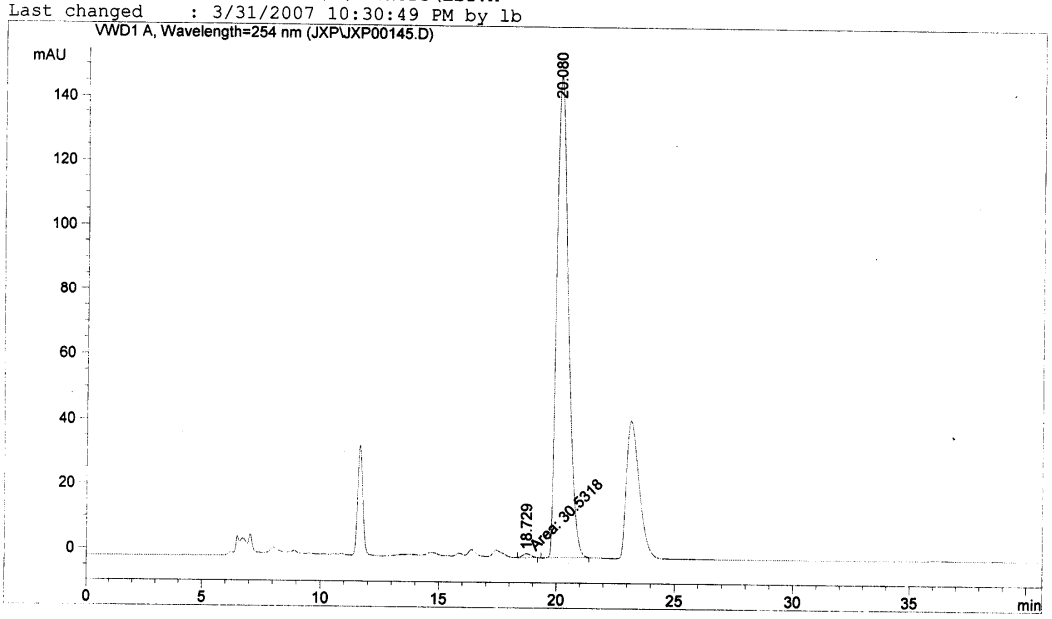


The HPLC spectrum of the mixture of (*S*)-*Z*-**2b** and (*R*)-*E*-**2b**

Data File D:\HPCHEM\1\DATA\JXP\JXP00145.D Sample Name: jxp-4-2-sx

Hex:i-PrOH=90/10; 0.5 ml/min; wavelength=254 nm; OJ-H

Injection Date : 3/29/2007 7:52:40 PM
Sample Name : jxp-4-2-sx Location : Vial 1
Acq. Operator : jxp
Acq. Method : D:\HPCHEM\1\METHODS\LB1.M
Last changed : 3/28/2007 11:19:44 AM by lb
Analysis Method : D:\HPCHEM\1\METHODS\LB1.M
Last changed : 3/31/2007 10:30:49 PM by lb



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.729	MM	0.4125	30.53183	1.23350	0.5908
2	20.080	VB	0.5327	5137.33154	149.22105	99.4092
Totals :				5167.86337	150.45455	

Results obtained with enhanced integrator!

*** End of Report ***

strument 1 4/1/2007 3:26:01 PM jxp Page 1 of 1

The HPLC spectrum of racemic *Z*-**2b**

Data File D:\HPCHEM\1\DATA\JXP\JXP00146.D Sample Name: jxp-2-79-wx

Hex:i-PrOH=90/10; 0.5 ml/min; wavelength=254 nm; OJ-H

```
==========================================================================
Injection Date  : 3/29/2007 8:38:20 PM
Sample Name     : jxp-2-79-wx                    Location : Vial 1
Acq. Operator   : jxp
Acq. Method     : D:\HPCHEM\1\METHODS\LB1.M
Last changed    : 3/28/2007 11:19:44 AM by lb
Analysis Method : D:\HPCHEM\1\METHODS\LB1.M
Last changed    : 3/31/2007 10:30:49 PM by lb
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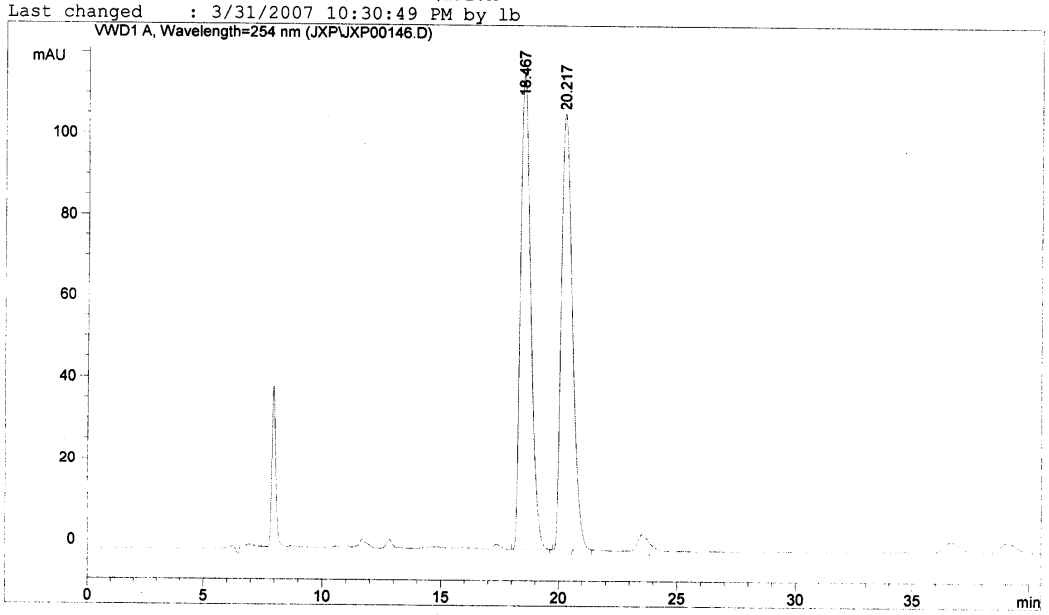


```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  18.467 BB    0.4658 3530.17065  116.91934  50.1132
   2  20.217 PB    0.5079 3514.22095  107.12416  49.8868

Totals :                  7044.39160  224.04350

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
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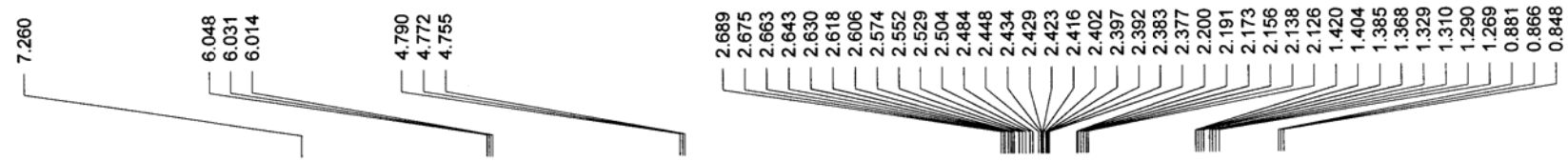
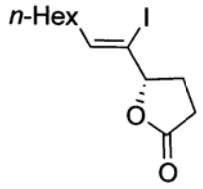
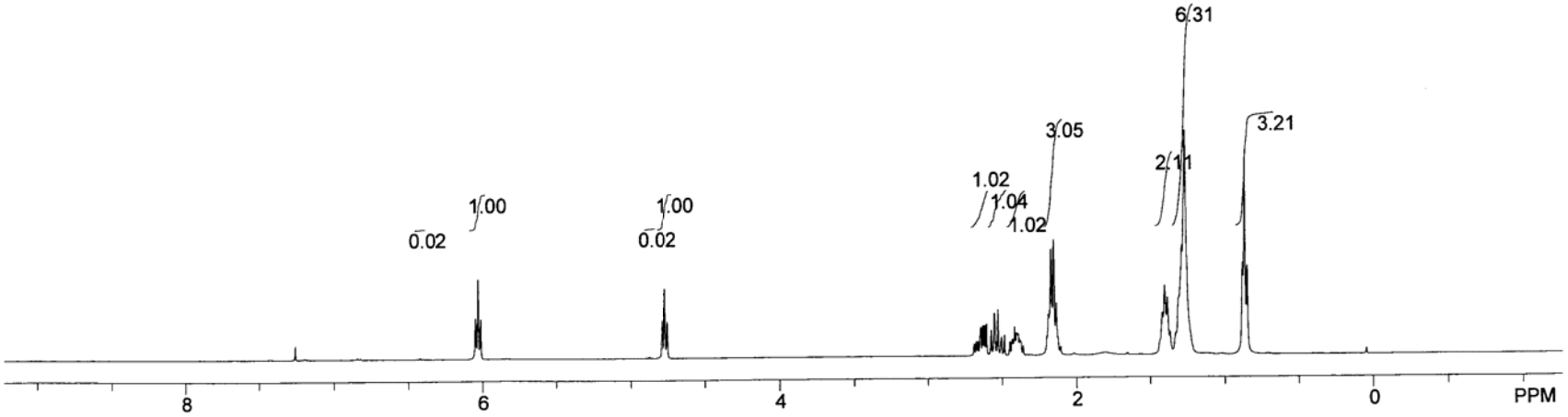
Instrument 1 4/1/2007 3:24:57 PM jxp Page 1 of 1





(*S*)-*Z*-**2a**

jxp-3-50-1



The HPLC spectrum of (*S*)-*Z*-**2a**

Data File D:\HPCHEM\1\DATA\JXP\JXP00098.D Sample Name: jxp-3-50-1

Hex:i-PrOH=90:10 0.5ml/min wavelength=254nm

```
Injection Date  : 11/30/2006 6:03:11 PM
Sample Name     : jxp-3-50-1                    Location : Vial 1
Acq. Operator   : jxp
Acq. Method     : D:\HPCHEM\1\METHODS\ZBC.M
Last changed    : 11/30/2006 3:41:58 PM by zbc
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\WM_LC.M
Last changed    : 6/9/2007 8:35:34 PM by zc
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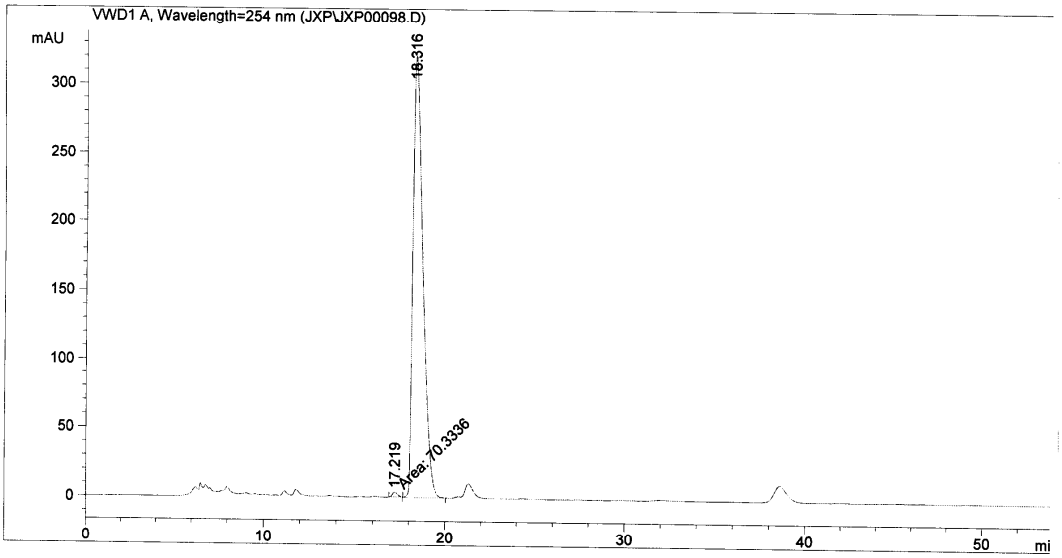


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                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  17.219 MM    0.3353   70.33362    3.49633   0.5714
   2  18.316 VB    0.5736 1.22393e4   320.57114  99.4286

Totals :                  1.23096e4   324.06747

 Results obtained with enhanced integrator!

                        *** End of Report ***
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Instrument 1 9/13/2007 2:29:19 PM lz

The HPLC spectrum of racemic *Z*-**2a**

Data File D:\HPCHEM\1\DATA\JXP\JXP00097.D Sample Name: jxp-3-56-w:

Hex:i-PrOH=90:10 0.5ml/min wavelength=254nm

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==========================================================================
Injection Date  : 11/30/2006 5:11:36 PM
Sample Name     : jxp-3-56-wx                    Location : Vial 1
Acq. Operator   : jxp
Acq. Method     : D:\HPCHEM\1\METHODS\ZBC.M
Last changed    : 11/30/2006 3:41:58 PM by zbc
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\WM_LC.M
Last changed    : 6/9/2007 8:35:34 PM by zc
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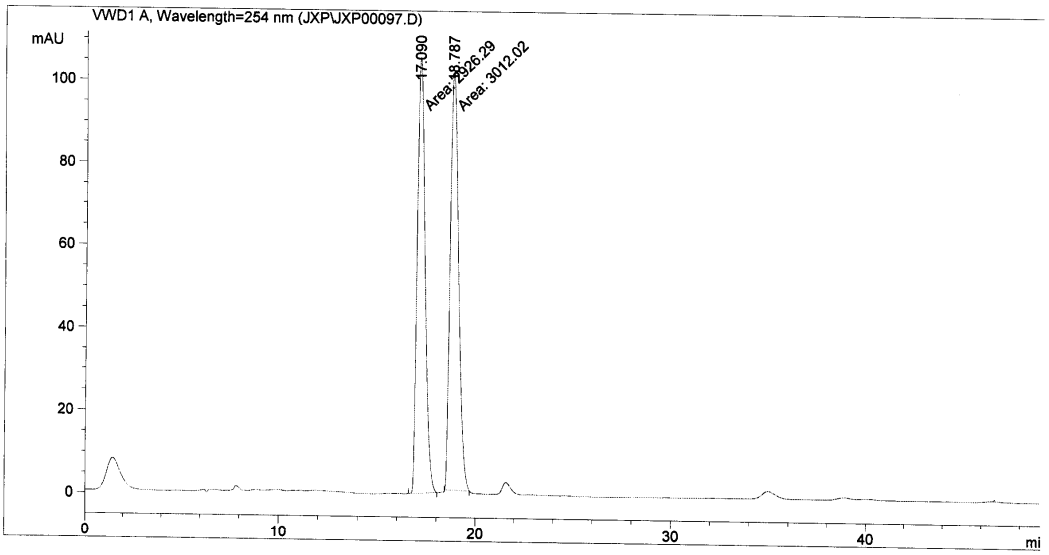


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==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  17.090 MM    0.4628 2926.29053  105.38081  49.2782
   2  18.787 MM    0.4971 3012.01611  100.98932  50.7218

Totals :                  5938.30664  206.37012

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
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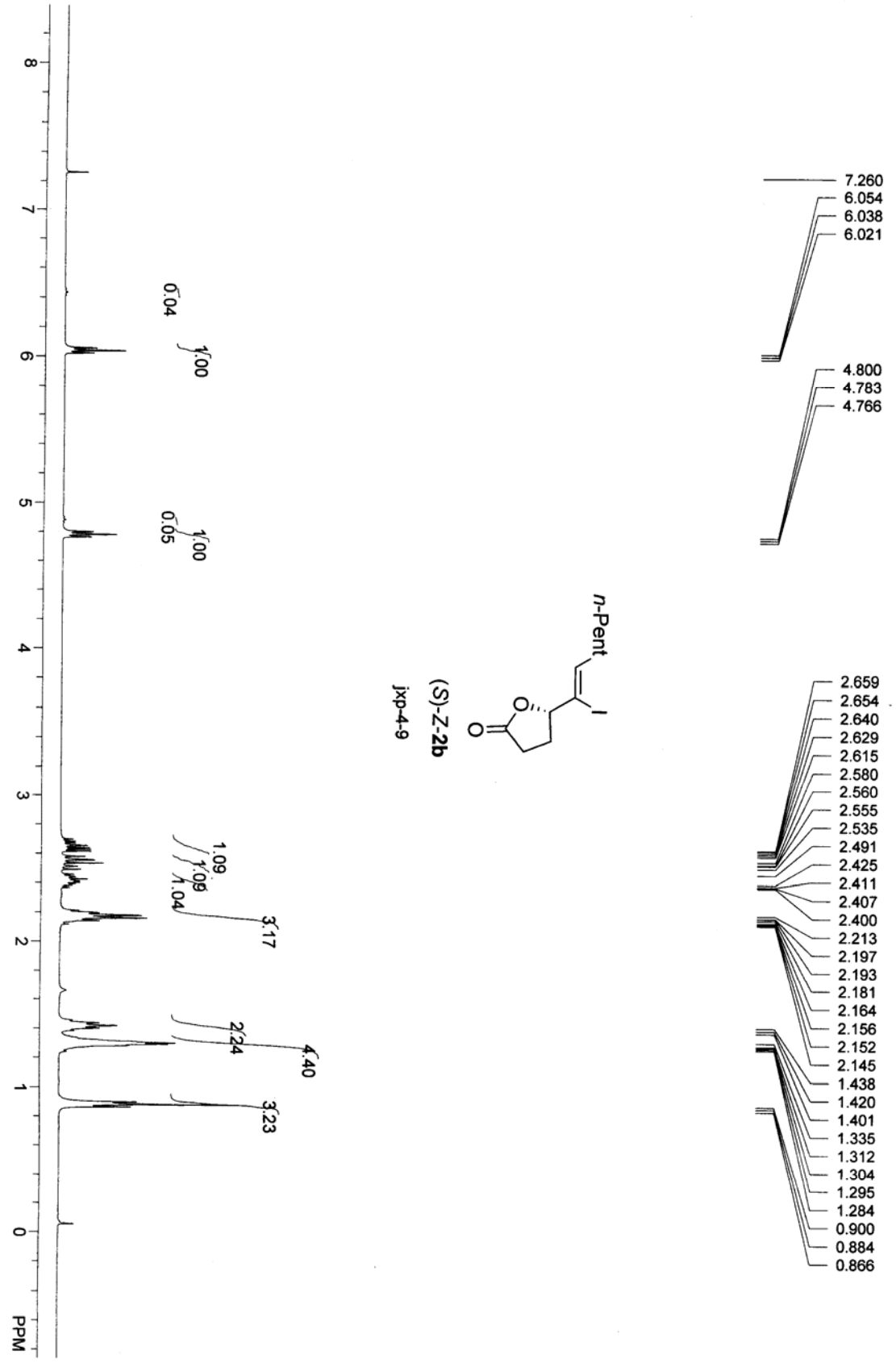
nstrument 1 9/13/2007 2:31:39 PM lz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2.555
2.535
2.491
2.425
2.411
2.407
2.400
2.213
2.197
2.193
2.181
2.164
2.156
2.152
2.145
1.438
1.420
1.401
1.335
1.312
1.304
1.295
1.284
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0.884
0.866
n-Pent
I
O
O
(S)-Z-2b
jxp-4-9
0.04
1.00
0.05
1.00
1.09
1.09
1.04
3.17
2.24
4.40
3.23
PPM

The HPLC spectrum of (*S*)-*Z*-**2b**

)ata File D:\HPCHEM\1\DATA\JXP\JXP00156.D Sample Name: jxp-4-9-sx

n-Hex/i-PrOH=90/10; 0.50ml/min; wavelength=254 nm; OJ-H

```
==========================================================================
Injection Date  : 4/1/2007 3:32:30 PM
Sample Name     : jxp-4-9-sx                    Location : Vial 1
Acq. Operator   : jxp
Method          : D:\HPCHEM\1\METHODS\LB1.M
Last changed    : 3/31/2007 10:30:49 PM by lb
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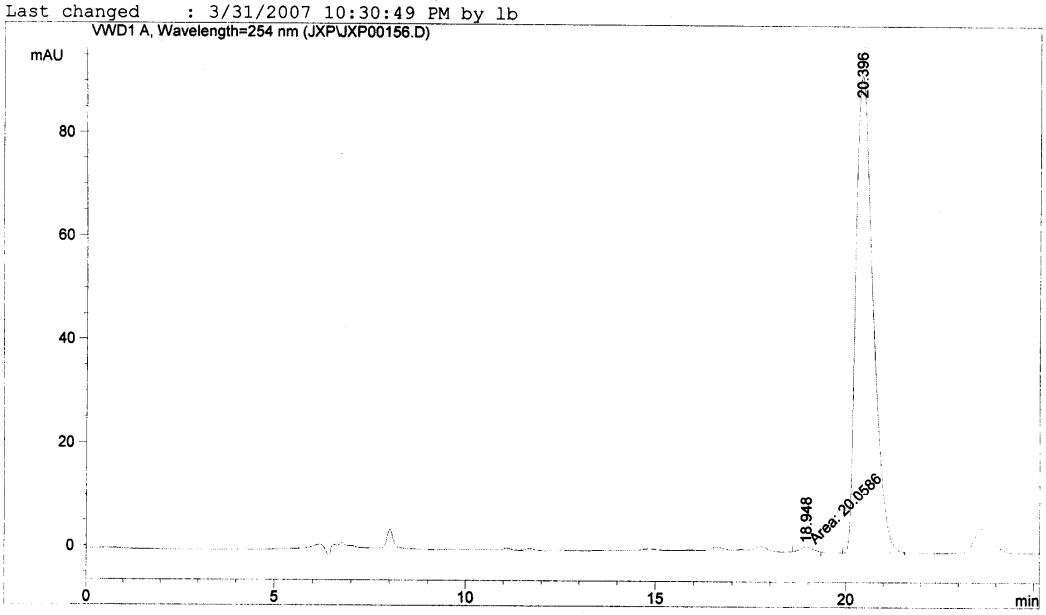


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==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  18.948 MM    0.3780   20.05861 8.84494e-1   0.6741
   2  20.396 PB    0.4954 2955.64355   92.41400  99.3259

Totals :                  2975.70217   93.29850

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

ıstrument 1 4/1/2007 4:00:25 PM jxp Page 1 of 1

The HPLC spectrum of racemic *Z*-**2b**

Data File D:\HPCHEM\1\DATA\JXP\JXP00146.D Sample Name: jxp-2-79-wx

Hex:i-PrOH=90/10; 0.5 ml/min; wavelength=254 nm; OJ-H

```
==========================================================================
Injection Date  : 3/29/2007 8:38:20 PM
Sample Name     : jxp-2-79-wx                    Location : Vial 1
Acq. Operator   : jxp
Acq. Method     : D:\HPCHEM\1\METHODS\LB1.M
Last changed    : 3/28/2007 11:19:44 AM by lb
Analysis Method : D:\HPCHEM\1\METHODS\LB1.M
Last changed    : 3/31/2007 10:30:49 PM by lb
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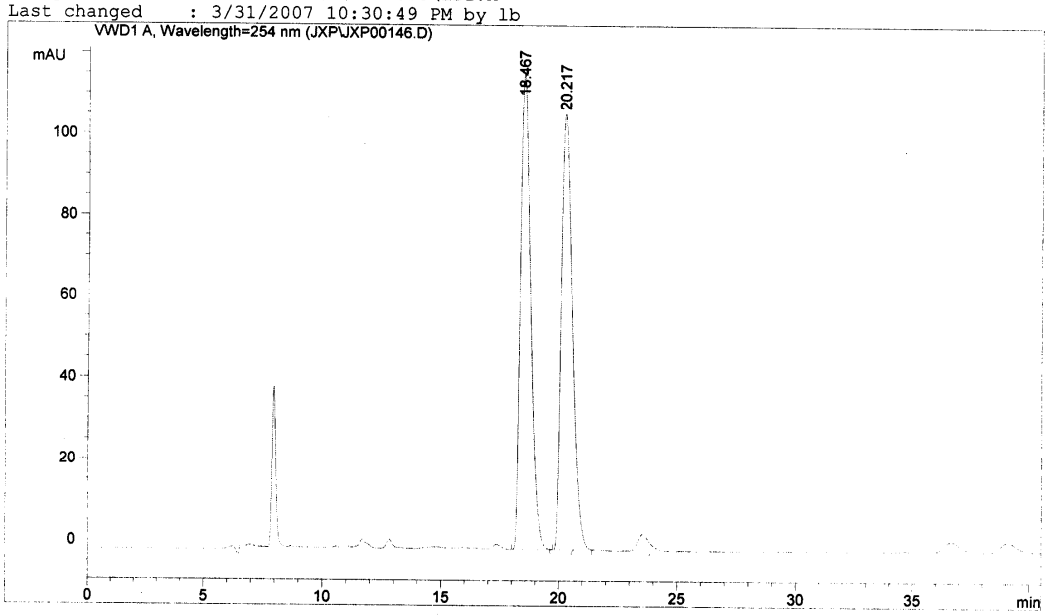



```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

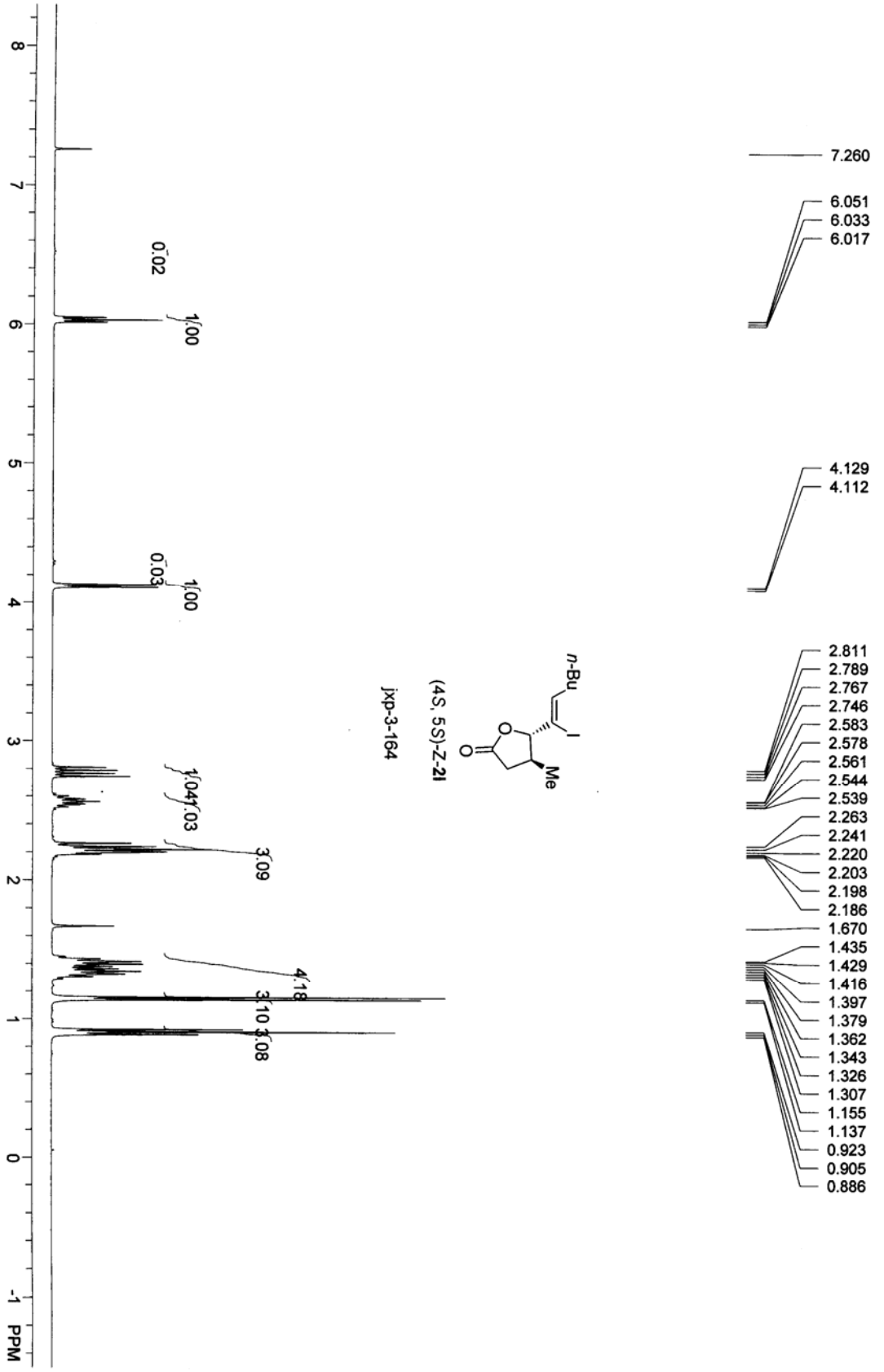
Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  18.467 BB    0.4658 3530.17065  116.91934  50.1132
   2  20.217 PB    0.5079 3514.22095  107.12416  49.8868

Totals :                  7044.39160  224.04350

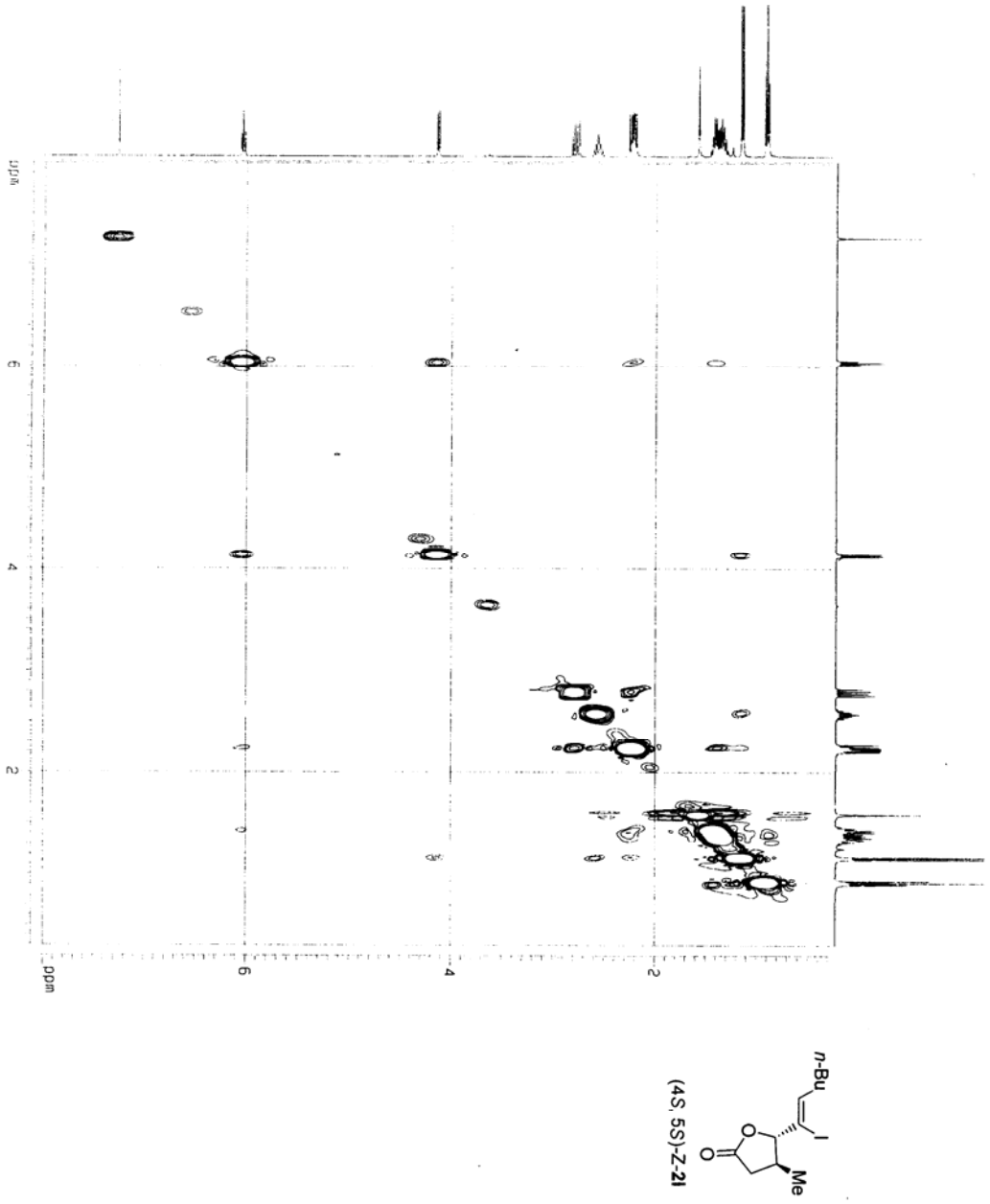
 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

Instrument 1 4/1/2007 3:24:57 PM jxp Page 1 of 1

The ^{1}H NMR spectrum of (4*S*, 5*S*)-*Z*-**2l** prepared from (*S*)-**1l**



NOESY spectrum of (4*S*, 5*S*)-*Z*-**2l** prepared from (*S*)-**1l**



The HPLC spectrum of (4*S*, 5*S*)-*Z*-**2l** prepared from (*S*)-**1l**

Data File D:\HPCHEM\1\DATA\JXP\JXP00139.D Sample Name: jxp-3-164-sx

Hex:i-PrOH=90/10; 0.5 ml/min; wavelength=254 nm; OJ-H

```
==========================================================================
Injection Date  : 3/3/2007 2:02:57 PM
Sample Name     : jxp-3-164-sx                  Location : Vial 1
Acq. Operator   : jxp
Acq. Method     : D:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 3/3/2007 10:10:13 AM by ZC
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\ERIC.M
Last changed    : 10/29/2007 4:06:59 PM by hgk
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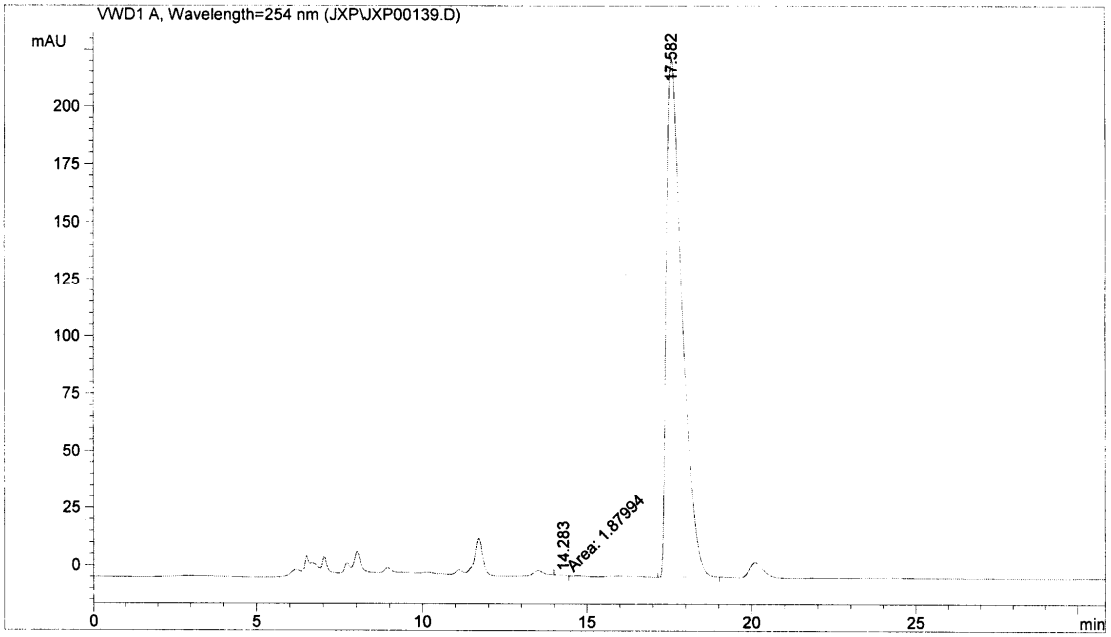


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==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  14.283 MM    0.2766    1.87994 1.13274e-1   0.0253
   2  17.582 PB    0.4943 7432.47119  226.00302  99.9747

Totals :                  7434.35113  226.11630

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

Instrument 1 1/27/2008 10:32:55 AM inuit Page 1 of 1

The HPLC spectrum of racemic-*trans*-*Z*-**21**

Data File D:\HPCHEM\1\DATA\JXP\JXP00138.D Sample Name: jxp-2-46

Hex:i-PrOH=90/10; 0.5 ml/min; wavelength=254 nm; OJ-H

```
Injection Date  : 3/3/2007 1:12:42 PM
Sample Name     : jxp-2-46                          Location : Vial 1
Acq. Operator   : jxp
Method          : D:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 3/3/2007 10:10:13 AM by ZC
                  (modified after loading)
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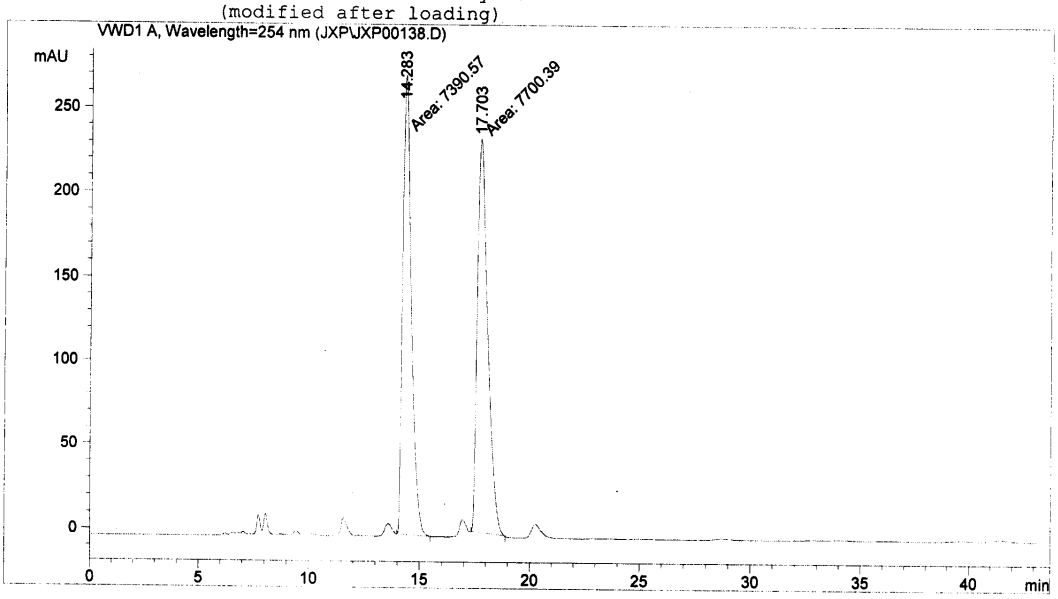


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                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

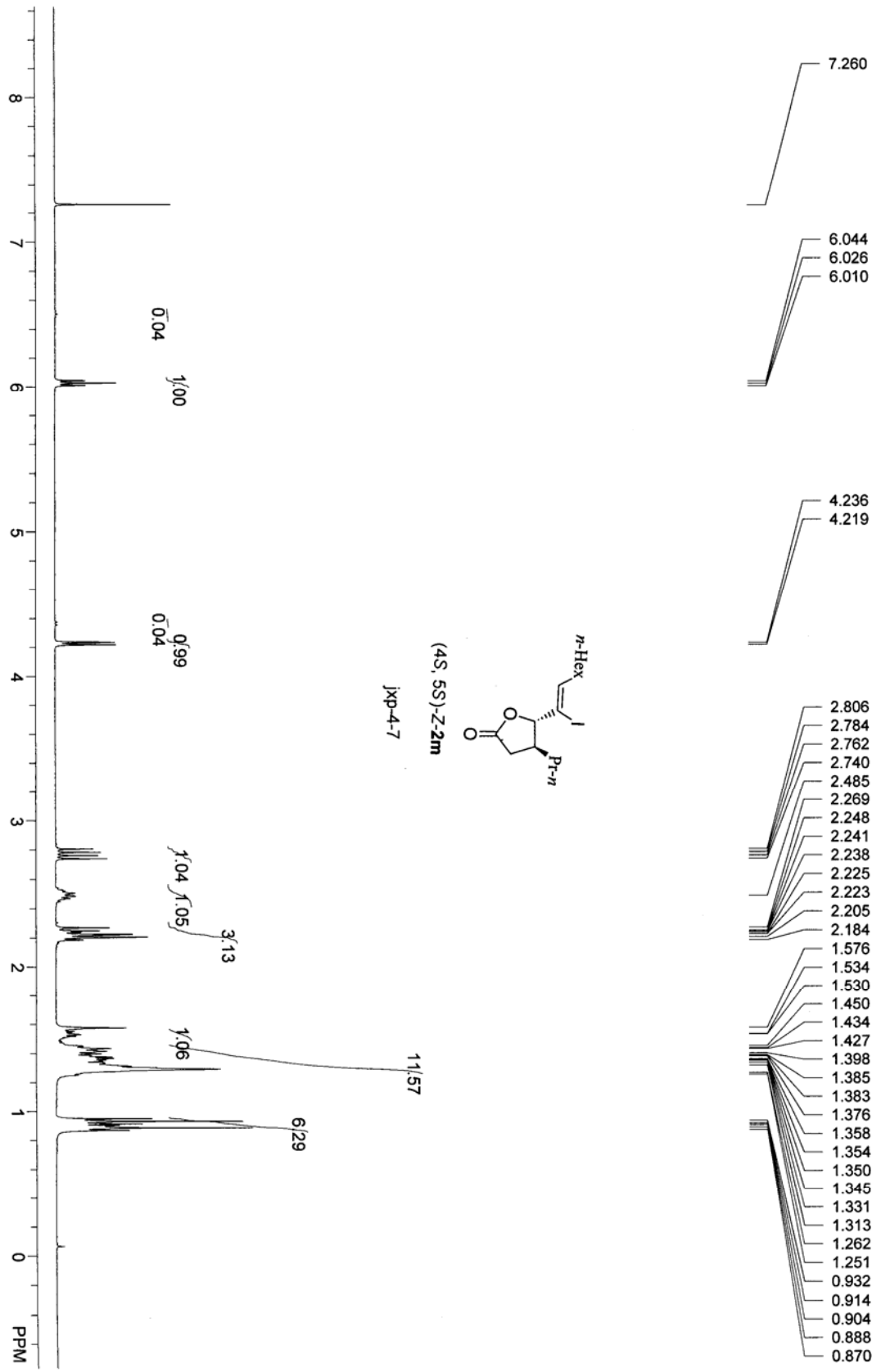
Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]  mAU   *s    [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1  14.283 MM    0.4510 7390.56836  273.12732  48.9735
   2  17.703 MM    0.5482 7700.39307  234.12288  51.0265

Totals :                  1.50910e4   507.25020

 Results obtained with enhanced integrator!

                          *** End of Report ***
```

Instrument 1 3/3/2007 3:35:39 PM jxp Page 1 of 1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2.241
2.238
2.225
2.223
2.205
2.184
1.576
1.534
1.530
1.450
1.434
1.427
1.398
1.385
1.383
1.376
1.358
1.354
1.350
1.345
1.331
1.313
1.262
1.251
0.932
0.914
0.904
0.888
0.870
n-Hex
I
Pr-n
O
O
(4S, 5S)-Z-2m
jxp-4-7
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1.00
0.99
0.04
1.04
1.05
3.13
1.06
11.57
6.29
PPM
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7
6
5
4
3
2
1
0

The HPLC spectrum of (4*S*, 5*S*)-*Z*-**2m**

Data File D:\HPCHEM\1\DATA\JXP\JXP00152.D Sample Name: jxp-4-7-sx

Hex:i-PrOH=95/5; 0.5 ml/min; wavelength=254 nm; OJ-H

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==========================================================================
Injection Date  : 3/30/2007 3:07:45 PM
Sample Name     : jxp-4-7-sx                    Location : Vial 1
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Last changed    : 3/30/2007 8:50:40 AM by jxp
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\LB1.M
Last changed    : 3/31/2007 10:30:49 PM by lb
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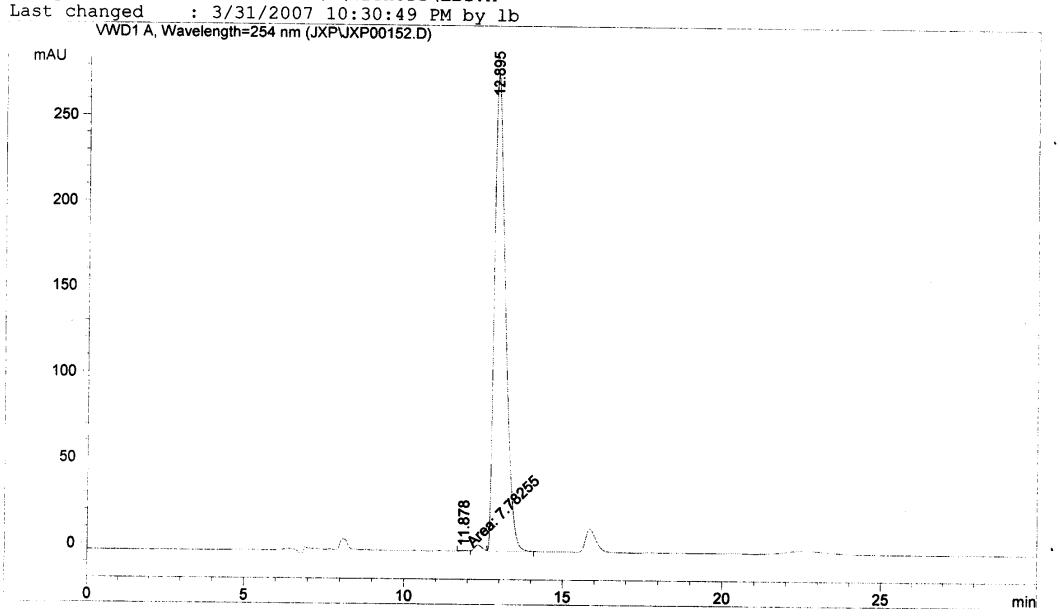


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==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  11.878 MM    0.2094    7.78255 4.58101e-1   0.1153
   2  12.895 VB    0.3694 6741.89014  278.85580  99.8847

Totals :                  6749.67268  279.31391

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

strument 1 4/1/2007 3:29:15 PM jxp Page 1 of 1

The HPLC spectrum of racemic *trans-Z*-**2m**

ata File D:\HPCHEM\1\DATA\JXP\JXP00151.D Sample Name: jxp-2-47-wx

Hex:i-PrOH=95/5; 0.5 ml/min; wavelength=254 nm; OJ-H

```
==========================================================================
Injection Date  : 3/30/2007 2:21:33 PM
Sample Name     : jxp-2-47-wx                    Location : Vial 1
Acq. Operator   : jxp
Acq. Method     : D:\HPCHEM\1\METHODS\LB1.M
Last changed    : 3/30/2007 8:50:40 AM by jxp
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\LB1.M
Last changed    : 3/31/2007 10:30:49 PM by lb
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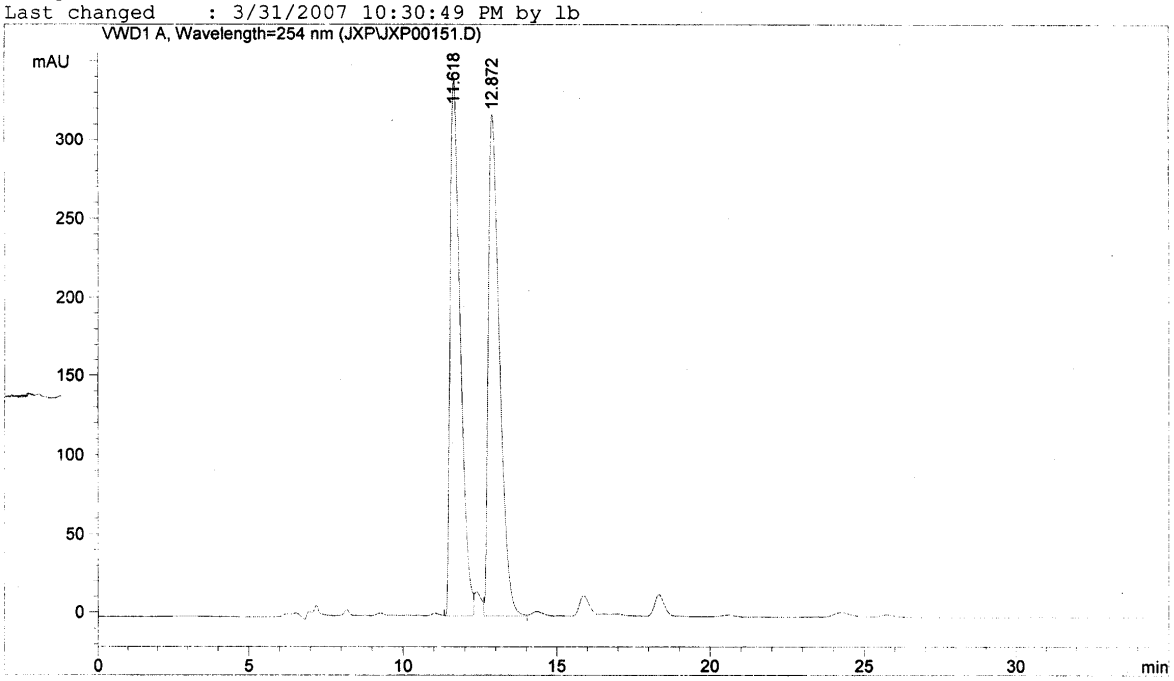


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==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

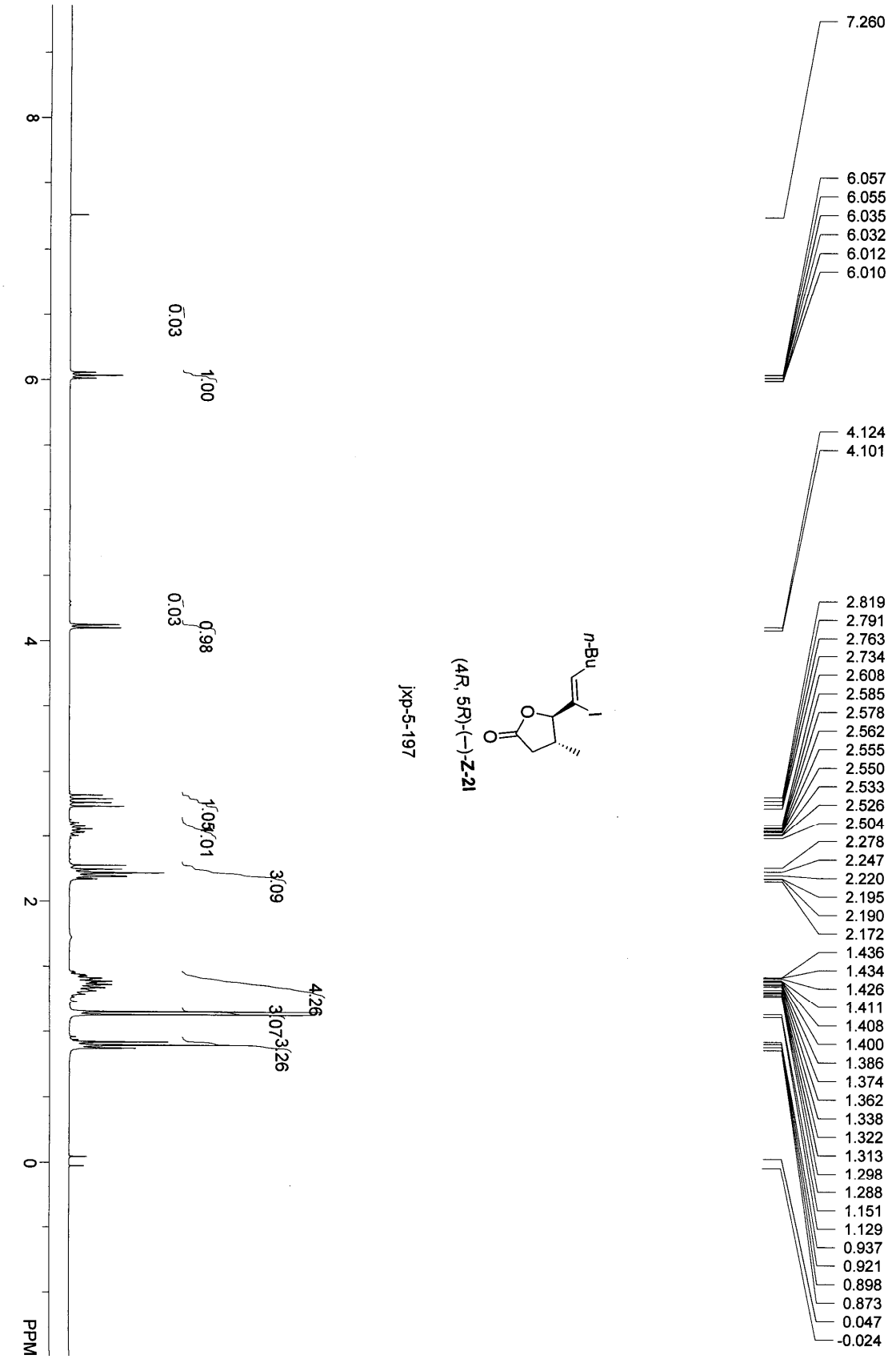
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  11.618 VV    0.3441 7789.97754  340.43665  49.1064
   2  12.872 VB    0.3815 8073.47461  318.68692  50.8936

Totals :                  1.58635e4   659.12357

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

nstrument 1 4/1/2007 3:28:13 PM jxp Page 1 of 1

The ^{1}H NMR spectrum of (4*R*, 5*R*)-(–)-*Z*-**2l** prepared from (*R*)-**1l**



The HPLC spectrum of (4*R*, 5*R*)-(–)-*Z*-**2l** prepared from (*R*)-**1l**

Data File D:\HPCHEM\1\DATA\JXP\JXP00189.D Sample Name: jxp-5-197-sx

n-hexane/i-propanol=90/10; 254 nm; 0.5 ml/min, OJ-H Chi
ral Pak

```
==========================================================================
Injection Date  : 3/12/2008 8:05:03 PM
Sample Name     : jxp-5-197-sx                  Location :   -
Acq. Operator   : jxp
Acq. Method     : D:\HPCHEM\1\METHODS\ERIC.M
Last changed    : 3/12/2008 7:53:23 PM by jxp
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Analysis Method : D:\HPCHEM\1\METHODS\ERIC.M
Last changed    : 5/19/2008 3:04:53 PM by wm
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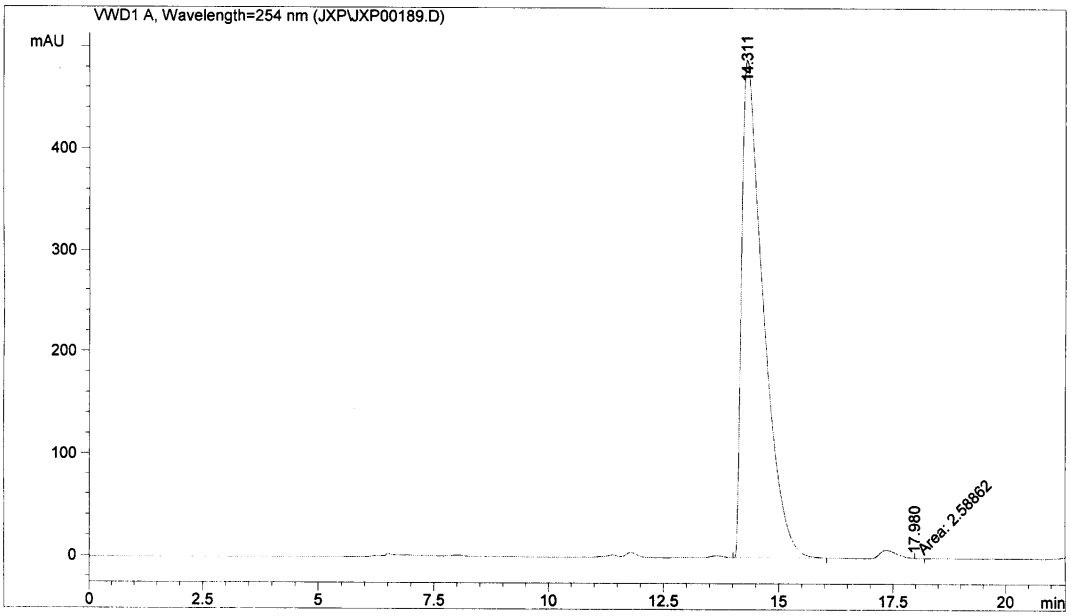


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==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  14.311 VP    0.4673 1.58087e4   489.22238  99.9836
   2  17.980 FM    0.1166    2.58862 3.70003e-1   0.0164

Totals :                  1.58113e4   489.59239

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

Instrument 1 5/23/2008 10:52:31 PM wm Page 1 of 1

The HPLC spectrum of racemic *trans*-*Z*-**2l**

Data File D:\HPCHEM\1\DATA\JXP\JXP00191.D Sample Name: jxp-5-194-w

n-hexane/i-propanol=90/10; 254 nm; 0.5 ml/min, OJ-H Chiral Pak

```
==========================================================================
Injection Date  : 3/12/2008 8:54:46 PM
Sample Name     : jxp-5-194-wx                    Location :   -
Acq. Operator   : jxp
Acq. Method     : D:\HPCHEM\1\METHODS\ERIC.M
Last changed    : 3/12/2008 7:53:23 PM by jxp
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\DEF_LC.M
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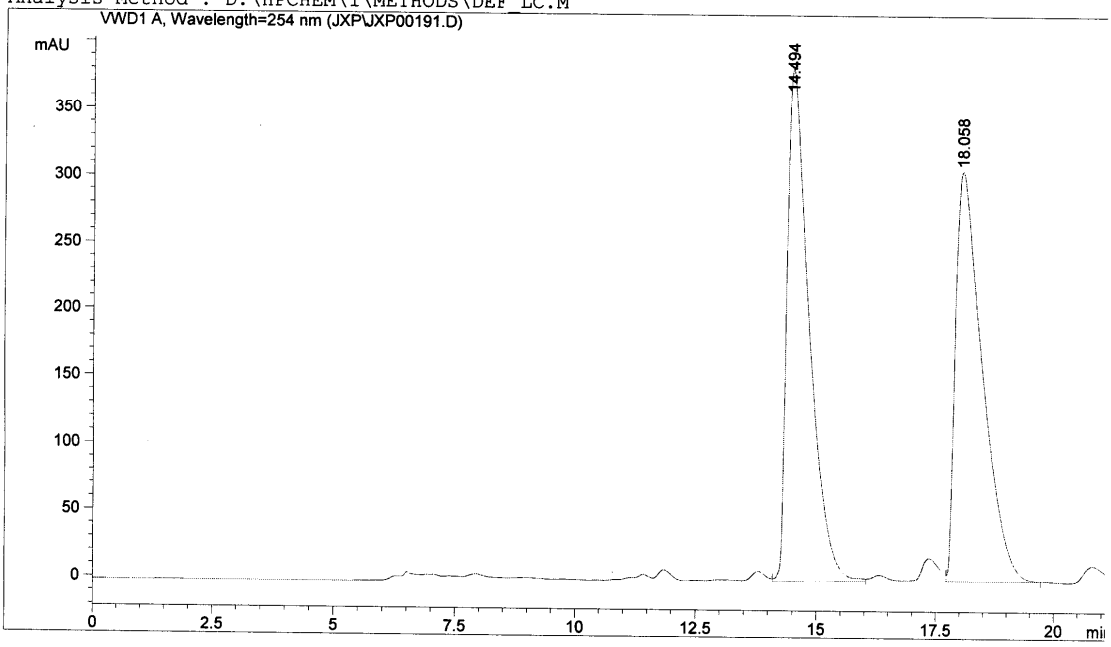


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==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

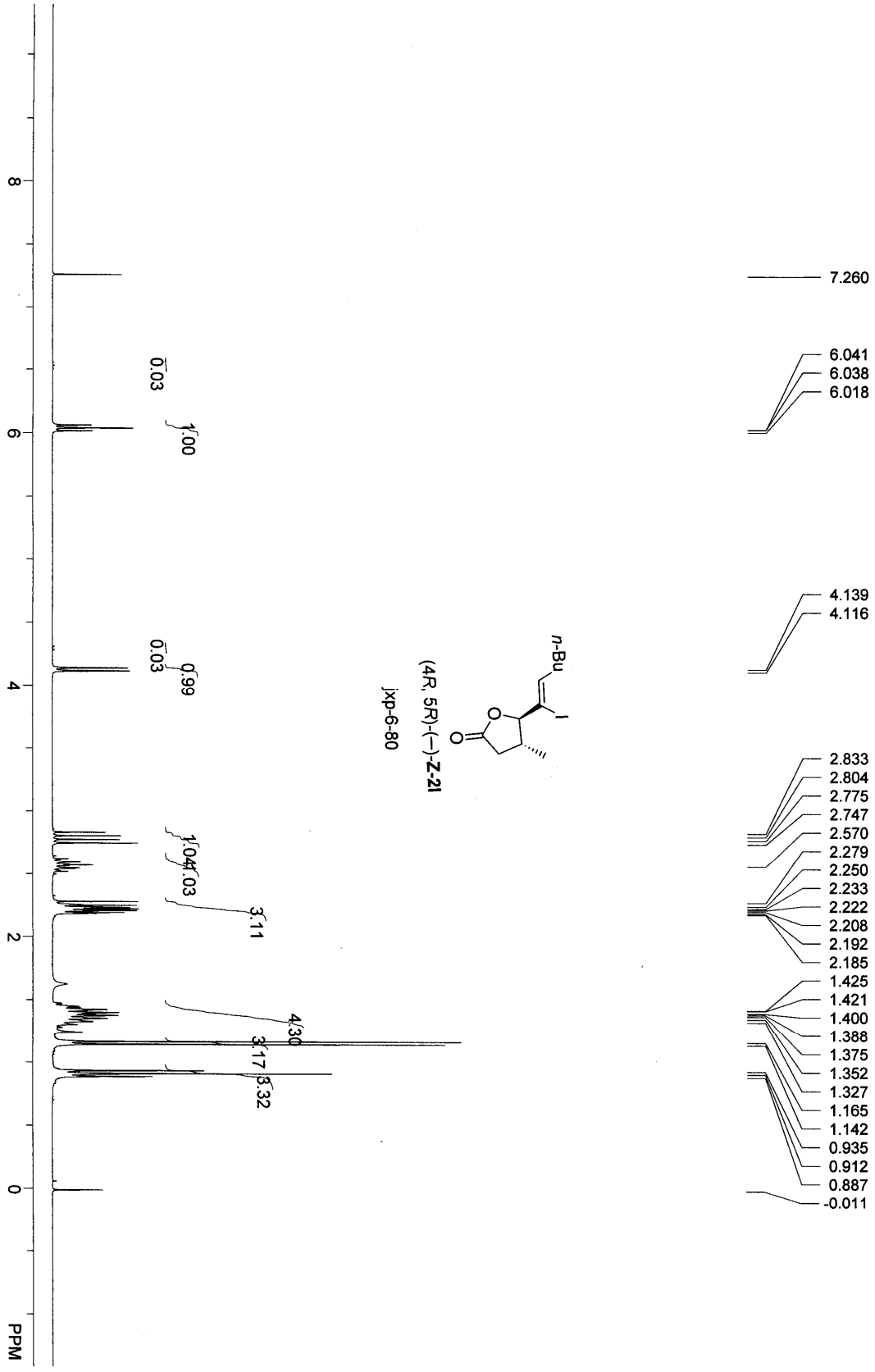
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.494 VV    0.4672 1.21809e4   382.95062  50.3296
   2  18.058 VB    0.5760 1.20214e4   306.18988  49.6704

Totals :                  2.42022e4   689.14050

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

Instrument 1 4/26/2008 7:32:20 PM mao Page 1 of 1

The ^{1}H NMR spectrum of (4*R*, 5*R*)-(–)-*Z*-**2l** prepared from (S_a, *R*)-(+)-**1l**

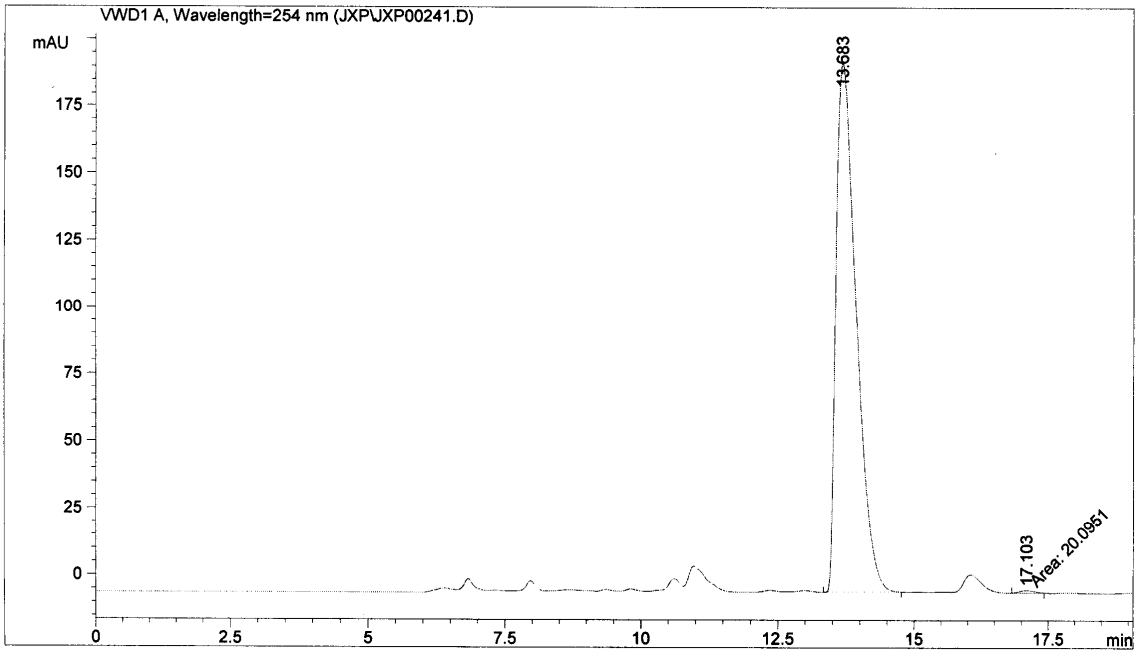


The HPLC spectrum of (4*R*, 5*R*)-(–)-*Z*-**2l** prepared from (S_a, *R*)-(+)-**1l**

Data File D:\HPCHEM\1\DATA\JXP\JXP00241.D Sample Name: jxp-6-80

n-hexane/i-propanol=90/10; 254nm; 0.5ml/min; OJ-H

```
==========================================================================
Injection Date  : 5/4/2008 12:24:42 PM
Sample Name     : jxp-6-80                      Location :   -
Acq. Operator   : jxp
Acq. Method     : D:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 5/4/2008 9:44:00 AM by hgk
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\ERIC.M
Last changed    : 5/9/2008 10:08:22 AM by sy
```

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==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  13.683 VB    0.3923 5068.64014  197.69995  99.6051
   2  17.103 MM    0.3453   20.09507 9.70058e-1   0.3949

Totals :                  5088.73521  198.67001

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Instrument 1 5/10/2008 4:35:26 PM wm Page 1 of 1

The HPLC spectrum of racemic *trans-Z*-**2l**

Data File D:\HPCHEM\1\DATA\JXP\JXP00242.D Sample Name: jxp-2-46-wx

n-hexane/i-propanol=90/10; 254nm; 0.5ml/min; OJ-H

```
==========================================================================
Injection Date  : 5/4/2008 2:19:25 PM
Sample Name     : jxp-2-46-wx                    Location :   -
Acq. Operator   : jxp
Acq. Method     : D:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 5/4/2008 9:44:00 AM by hgk
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\ERIC.M
Last changed    : 5/9/2008 10:08:22 AM by sy
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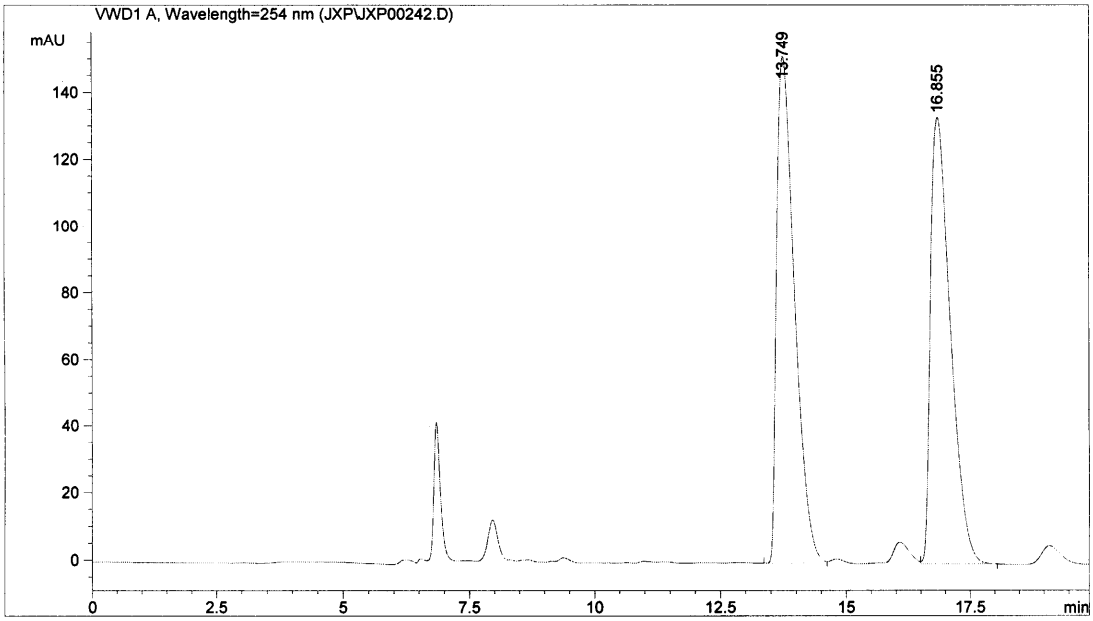


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==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

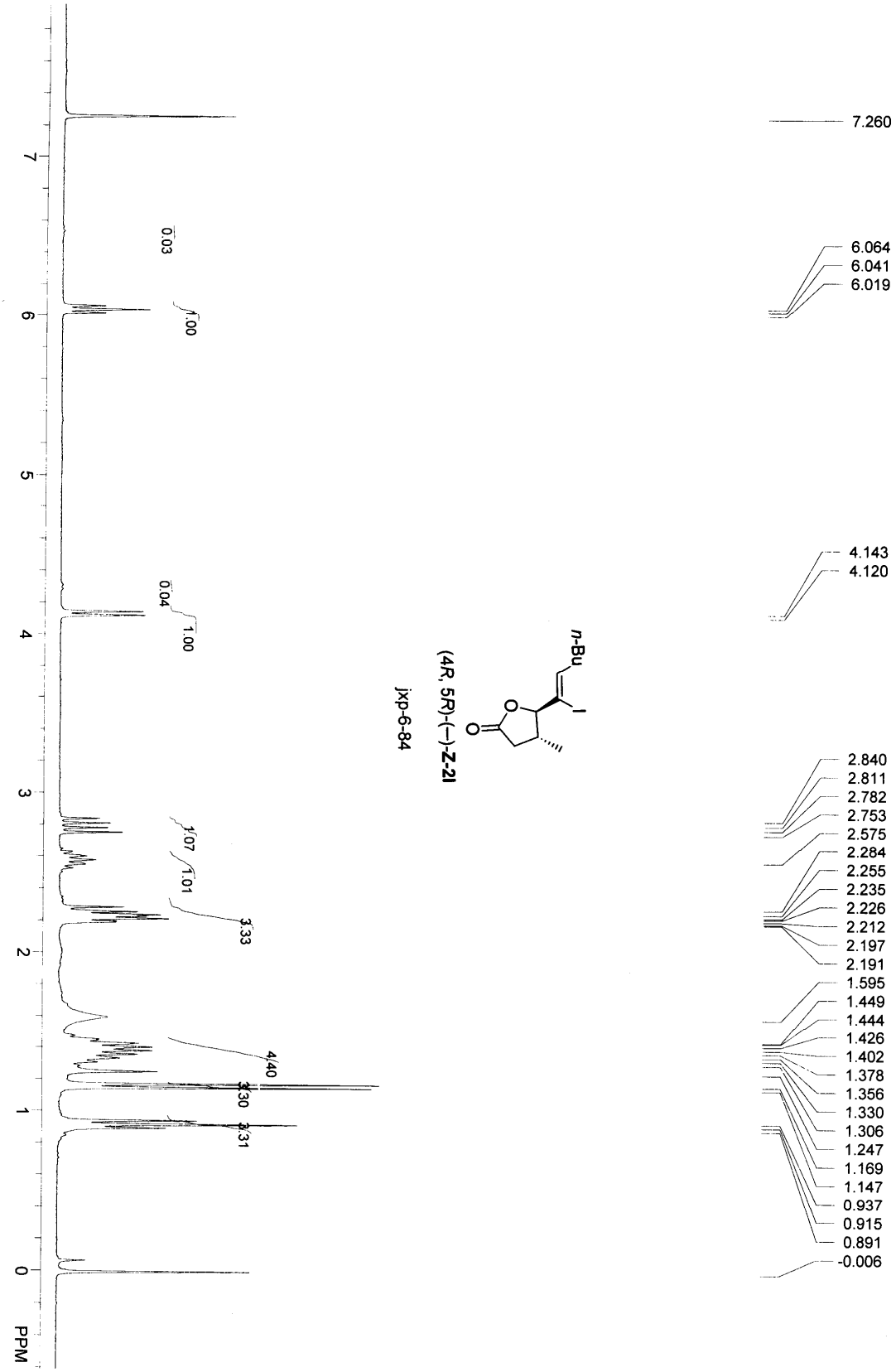
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  13.749 BV    0.3845 3749.45728  151.65854  50.0056
   2  16.855 VB    0.4351 3748.62085  133.60046  49.9944

Totals :                  7498.07812  285.25900

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Instrument 1 5/10/2008 4:29:50 PM wm Page 1 of 1

The ^{1}H NMR spectrum of (4*R*, 5*R*)-(–)-*Z*-**2l** prepared from (R_a, *R*)-(+)-**1l**

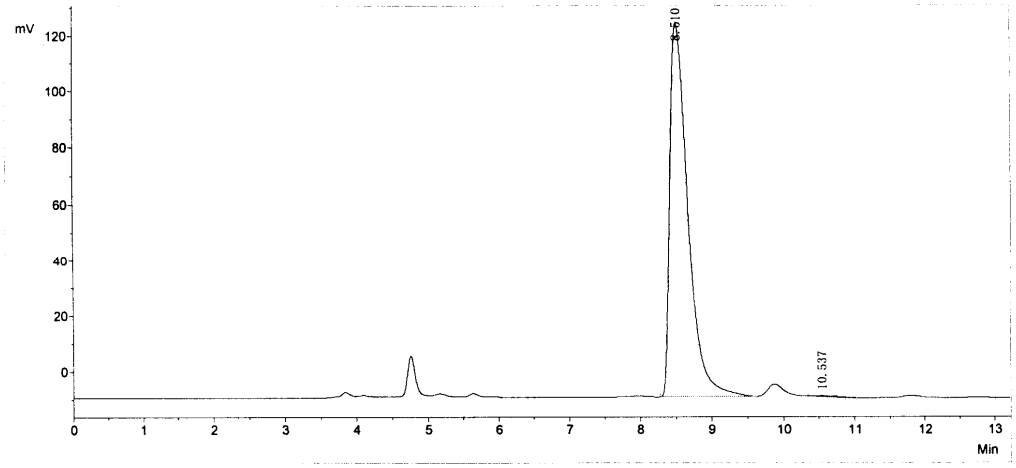


The HPLC spectrum of (4*R*, 5*R*)-(–)-*Z*-**2l** prepared from (R_a, *R*)-(+)-**1l**

HPLC REPORT

Sample Name:jxp-6-84-sx.che
Time:16:37
column: OJ-H (150mm)
Velocity: 0.5ml/min

Date:2008-05-08
Method:
the mobile phase: Hex:i-PrOH = 90/10
the detection wavelength: 254nm



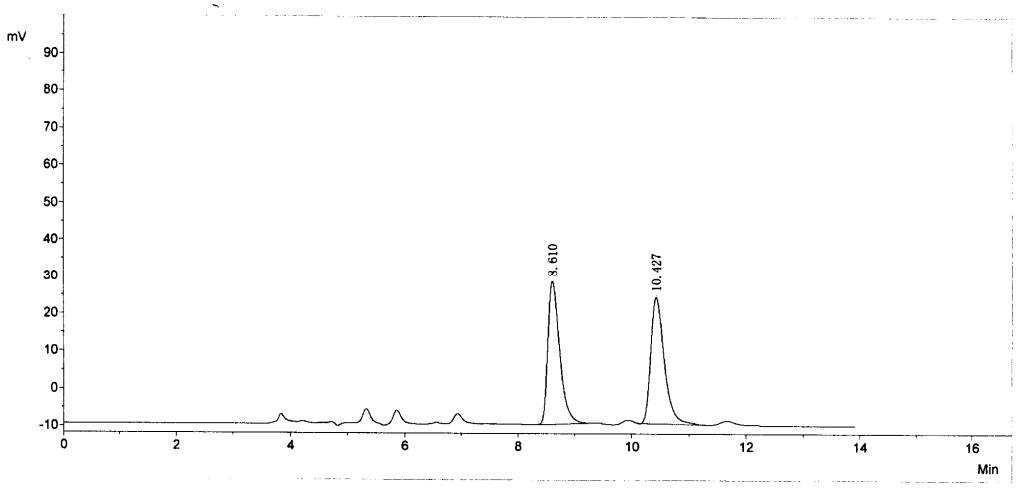
No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	8.510	132998.4	2330054.1	99.8062
2	2	10.537	204.1	4523.5	0.1938
Total			133202.5	2334577.6	100.0000

The HPLC spectrum of racemic *trans-Z*-**2l**

HPLC REPORT

Sample Name:jxp-2-46-wx oj 90 0.5.che
Time:16:22
column: OJ-H (150mm).
Velocity: 0.5ml/min.

Date:2008-05-08
Method:
the mobile phase: Hex:i-PrOH=90/10.
the detection wavelength: 254nm.



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	8.610	38066.3	551583.3	49.7431
2	2	10.427	33629.1	557279.7	50.2569
Total			71695.4	1108863.0	100.0000