Synthesis of Highly Substituted Allylic Alcohols by a Regio- and Stereo-defined CuCl-Mediated Carbometallation Reaction of 3-Aryl Substituted Secondary Propargylic Alcohols with Grignard Reagents

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Experimental Section

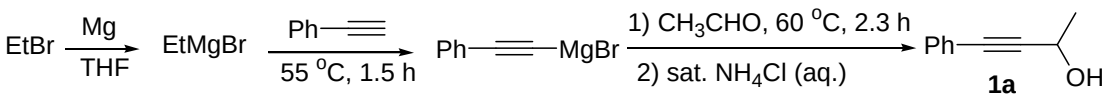
Materials. Et_2O and THF were distilled from Na/benzophenone, Et_3N was distilled from KOH, and DMSO was distilled from CaH_2. The commercially available chemicals were purchased and used without additional purification unless otherwise noted. Melting points were determined by a semi automatic melting point apparatus made by Shenguang in China.

1. Synthesis of 3-Aryl Substituted Secondary Propargylic Alcohols

General Procedure for Synthesis of 1a-d:[1]

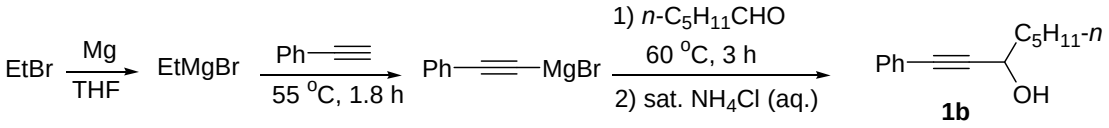
To a dry three-necked flask containing the magnesium turnings (2.88 g, 0.12 mol) and I_2 (a few crystals) in THF (120 mL) were added several drops of ethyl bromide. Upon the initiation of the Grignard reaction, the remaining ethyl bromide (0.12 mol) was added dropwise, which was followed by stirring until the magnesium disappeared. Phenylethyne (0.10 mol) was added dropwise into the solution at 55 ^oC followed by stirring for 1.5 h at this temperature. Then corresponding aldehyde (fresh distilled) or acetone (0.08 mol) was added at 55 ^oC and the resulting mixture was stirred at this temperature for 2 h. The reaction mixture was then quenched with an aqueous solution of saturated NH_4Cl and extracted with Et_2O. The combined organic layer was washed with 5 % HCl, sat. $NaHCO_3$ (aq.), brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation of the solvent, and distillation afforded the propargylic alcohols.

(1) 4-Phenyl-3-butyn-2-ol (1a)



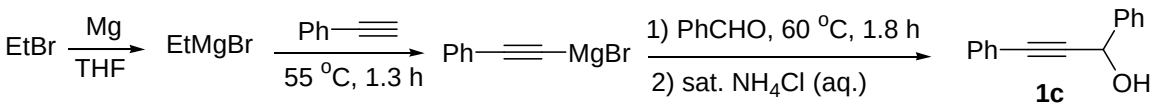
The reaction of ethyl bromide (8.96 mL, *d* = 1.461 g/mL, 13.09 g, 0.12 mol), magnesium turnings (2.88 g, 0.12 mol), phenylethyne (11.0 mL, *d* = 0.930 g/mL, 10.20 g, 0.10 mol), and acetaldehyde (4.0 mL, *d* = 0.780 g/mL, 3.12 g, 0.07 mol) in THF (120 mL) afforded **1a**[2] (8.72 g, 84%, 126-128 °C/2.2 mmHg): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.38 (m, 2 H), 7.33-7.27 (m, 3 H), 4.81-4.72 (m, 1 H), 2.24 (bs, 1 H), 1.55 (d, *J* = 6.6 Hz, 3 H).

(2) 1-Phenyl-1-octyn-3-ol (1b)



The reaction of ethyl bromide (8.96 mL, *d* = 1.461 g/mL, 13.09 g, 0.12 mol), magnesium turnings (2.88 g, 0.12 mol), phenylethyne (11.0 mL, *d* = 0.930 g/mL, 10.20 g, 0.10 mol), and hexanal (9.9 mL, *d* = 0.834 g/mL, 8.23 g, 0.08 mol) in THF (120 mL) afforded **1b**[3] (11.12 g, 67%, 165.5 °C/10.5 mmHg): Liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.41 (m, 2 H), 7.35-7.27 (m, 3 H), 4.61 (t, *J* = 6.8 Hz, 1 H), 2.35-2.15 (m, 1 H), 1.88-1.74 (m, 2 H), 1.60-1.44 (m, 2 H), 1.40-1.28 (m, 4 H), 0.92 (t, *J* = 6.2 Hz, 3 H).

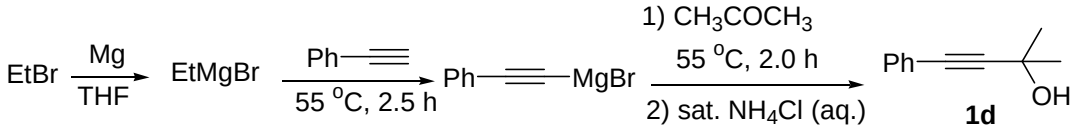
(3) 1,3-Diphenyl-2-propyn-1-ol (1c)



The reaction of ethyl bromide (6.9 mL, *d* = 1.461 g/mL, 10.08 g, 0.09 mol), magnesium turnings (2.10 g, 0.09 mol), phenylethyne (8.8 mL, *d* = 0.930 g/mL, 8.18 g, 0.08 mol), and benzaldehyde (8.2 mL, *d* = 1.045 g/mL, 8.57 g, 0.08 mol) in THF (70 mL) afforded **1c**[4] (13.55 g, 81%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ

7.63-7.56 (m, 2 H), 7.49-7.41 (m, 2 H), 7.40-7.25 (m, 6 H), 5.66 (s, 1 H), 2.59 (bs, 1 H).

(4) 2-Methyl-4-phenyl-3-butyn-2-ol (1d)

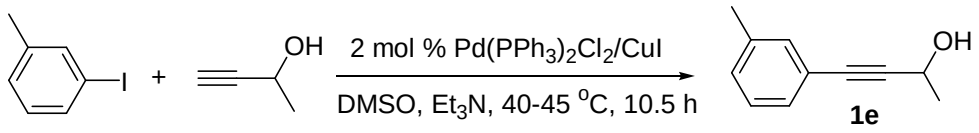


The reaction of ethyl bromide (0.90 mL, d = 1.461 g/mL, 1.31 g, 0.012 mol), magnesium turnings (0.29 g, 0.012 mol), phenylethyne (1.1 mL, d = 0.930 g/mL, 1.02 g, 0.01 mol), and acetone (0.59 mL, d = 0.791 g/mL, 0.47 g, 0.008 mol) in THF (12 mL) afforded a crude product, which was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to afford **1d**[5] (1.22 g, 94%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.38 (m, 2 H), 7.32-7.25 (m, 3 H), 2.364 (s, 1 H), 1.62 (s, 6 H).

General Procedure for the Synthesis of 1e-k:[6]

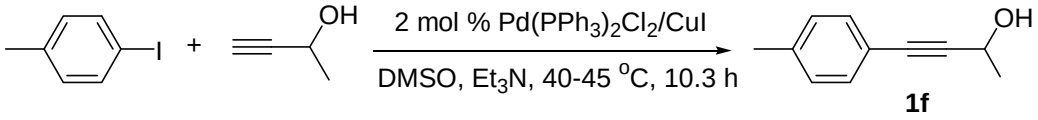
To a dry three-necked flask were added aryl iodide (2 mmol), 3-butyn-2-ol (4 mmol, 2 equiv), CuI (2 mol%), $Pd(PPh_3)_2Cl_2$ (2 mol%), DMSO (5 mL), and Et_3N (5 mL). The resulting mixture was then heated at 40-45 ^{o}C. After complete conversion of the starting material as monitored by TLC, the reaction mixture was quenched with an aqueous solution of saturated NH_4Cl and extracted with Et_2O. The combined organic layer was washed with 5 % HCl, sat. $NaHCO_3$ (aq.), brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1~2/1) afforded the desired product.

(1) 4-(*m*-Methylphenyl)-3-butyn-2-ol (1e)



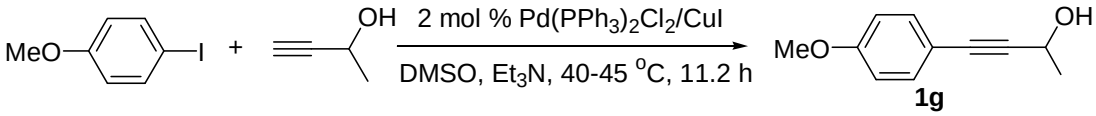
The reaction of 3-iodotoluene (1.0959 g, 5.0 mmol), 3-butyn-2-ol (0.6983 g, 9.9 mmol), CuI (0.0193 g, 0.10 mmol, 2 mol%), and $Pd(PPh_3)_2Cl_2$ (0.0675 g, 0.096 mmol, 2 mol%) in 12 mL of DMSO and 10 mL of Et_3N afforded **1e**[7] (0.7166 g, 89%): Liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.27-7.08 (m, 4 H), 4.80-4.70 (m, 1 H), 2.32 (d, J = 0.3 Hz, 3 H), 2.04-1.98 (m, 1 H), 1.55 (d, J = 6.6 Hz, 3 H).

(2) 4-(*p*-Methylphenyl)-3-butyn-2-ol (1f)



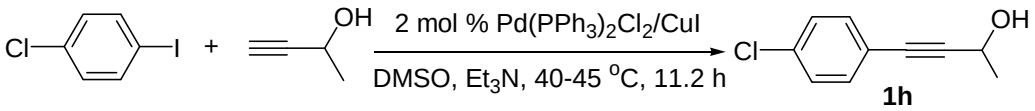
The reaction of 4-iodotoluene (1.1127 g, 5.1 mmol), 3-butyn-2-ol (0.7260 g, 10.4 mmol), CuI (0.0202 g, 0.11 mmol, 2 mol%), and $Pd(PPh_3)_2Cl_2$ (0.0722 g, 0.10 mmol, 2 mol%) in 20 mL of DMSO and 20 mL of Et_3N afforded **1f**[7] (0.7458 g, 91%): Liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2 H), 7.12-7.07 (m, 2 H), 4.80-4.70 (m, 1 H), 2.42 (bs, 1 H), 2.33 (s, 3 H), 1.54 (d, J = 6.6 Hz, 3 H).

(3) 4-(*p*-Methoxyphenyl)-3-butyn-2-ol (1g)



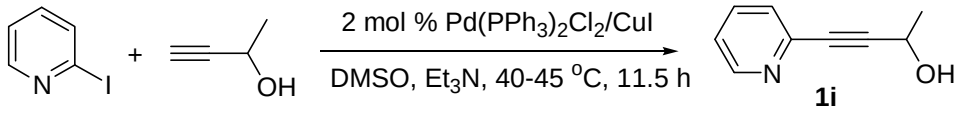
The reaction of 4-iodoanisole (0.4880 g, 2.1 mmol), 3-butyn-2-ol (0.2808 g, 4.0 mmol), CuI (0.0080 g, 0.04 mmol, 2 mol%), and $Pd(PPh_3)_2Cl_2$ (0.0284 g, 0.04 mmol, 2 mol%) in 5 mL of DMSO and 5 mL of Et_3N afforded **1g**[7] (0.2863 g, 78%): Liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39-7.34 (m, 2 H), 6.86-6.80 (m, 2 H), 4.80-4.70 (m, 1 H), 3.81 (s, 3 H), 2.01 (d, J = 4.5 Hz, 1 H), 1.54 (d, J = 6.6 Hz, 3 H).

(4) 4-(*p*-Chlorophenyl)-3-butyn-2-ol (1h)



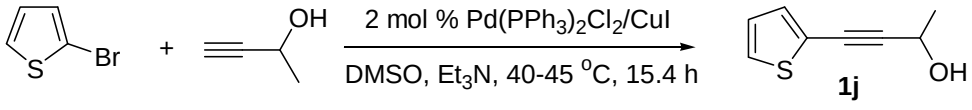
The reaction of 4-chloroiodobenzene (0.4792 g, 2.0 mmol), 3-butyn-2-ol (0.2737 g, 3.9 mmol), CuI (0.0084 g, 0.044 mmol, 2 mol%), $Pd(PPh_3)_2Cl_2$ (0.0279 g, 0.039 mmol, 2 mol%) in 8 mL of DMSO and 8 mL of Et_3N afforded **1h**[7] (0.3376 g, 93%): Liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38-7.33 (m, 2 H), 7.31-7.26 (m, 2 H), 4.80-4.70 (m, 1 H), 2.02-1.96 (m, 1 H), 1.55 (d, J = 6.6 Hz, 3 H).

(5) 4-(2-Pyridyl)-3-butyn-2-ol (1i)



The reaction of 2-iodopyridine (0.4148 g, 2.0 mmol), 3-butyn-2-ol (0.2832 g, 4.0 mmol), CuI (0.0082 g, 0.043 mmol, 2 mol%), and $Pd(PPh_3)_2Cl_2$ (0.0280 g, 0.040 mmol, 2 mol%) in 5 mL of DMSO and 5 mL of Et_3N afforded **1i**[8] (0.2801 g, 94%). The reaction mixture was extracted with ethyl acetate and washed with brine. **1i**: Liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 8.58-8.54 (m, 1 H), 7.65 (td, J = 7.7 and 1.5 Hz, 1 H), 7.43-7.38 (m, 1 H), 7.27-7.20 (m, 1 H), 4.86-4.76 (m, 1 H), 3.56 (d, J = 5.1 Hz, 1 H), 1.59 (d, J = 6.6 Hz, 3 H).

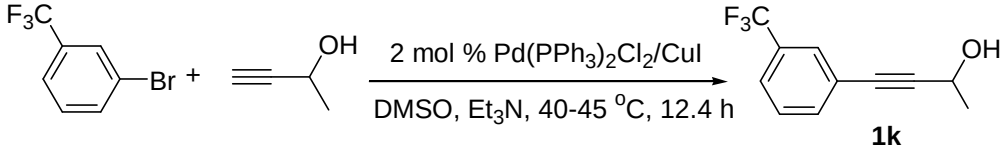
(6) 4-(2-Thienyl)-3-butyn-2-ol (1j)



The reaction of 2-bromothiophene (0.3548 g, 2.2 mmol), 3-butyn-2-ol (0.2792 g, 4.0 mmol), CuI (0.0099 g, 0.052 mmol, 2 mol%), and $Pd(PPh_3)_2Cl_2$ (0.0283 g, 0.040 mmol, 2 mol%) in 5 mL of DMSO and 5 mL of Et_3N afforded **1j**[9] (0.1921 g, 58%):

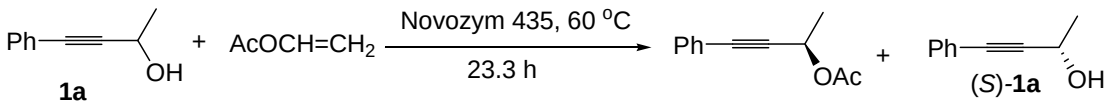
Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 1.2 Hz, 1 H), 7.20 (dd, *J* = 3.6 and 1.2 Hz, 1 H), 6.99-6.95 (m, 1 H), 4.81-4.72 (m, 1 H), 2.01-1.95 (m, 1 H), 1.55 (d, *J* = 6.6 Hz, 3 H).

(7) 4-(*m*-Trifluoromethylphenyl)-3-butyn-2-ol (1k)



The reaction of 3-trifluoromethylphenyl bromide (0.4577 g, 2.0 mmol), 3-butyn-2-ol (0.2772 g, 4.0 mmol), CuI (0.0092 g, 0.048 mmol, 2 mol%), and $Pd(PPh_3)_2Cl_2$ (0.0296 g, 0.042 mmol, 2 mol%) in 5 mL of DMSO and 5 mL of Et_3N afforded **1k** (0.3224 g, 74%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (s, 1 H), 7.61-7.51 (m, 2 H), 7.46-7.39 (m, 1 H), 4.82-4.73 (m, 1 H), 2.20-2.08 (m, 1 H), 1.57 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 134.7, 130.9 (q, *J* = 32.4 Hz, 1 C), 128.8, 128.4 (q, *J* = 3.6 Hz, 1 C), 124.9 (q, *J* = 3.7 Hz, 1 C), 123.6 (q, *J* = 270.8 Hz), 123.5, 92.5, 82.5, 58.7, 24.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -63.0; IR (neat, cm^{-1}) 3341, 2985, 2934, 1610, 1588, 1487, 1432, 1372, 1335, 1237, 1169, 1130, 1073, 1039; MS (m/z) 214 (M^+, 10.52), 199 (100), HRMS calcd for $C_{11}H_9F_3O$ (M^+): 214.0605, found: 214.0604.

2. Synthesis of Optically Active Propargylic Alcohol (*S*)-4-Phenyl-3-butyn-2-ol ((*S*)-1a) from Racemic Propargylic Alcohol 1a[10,11]



To a mixture of racemic **1a** (4.0032 g) and vinyl acetate (100 mL) was added Novozym 435 (0.7008 g). After shaking at 60 °C for 23.3 h as monitored by TLC, the

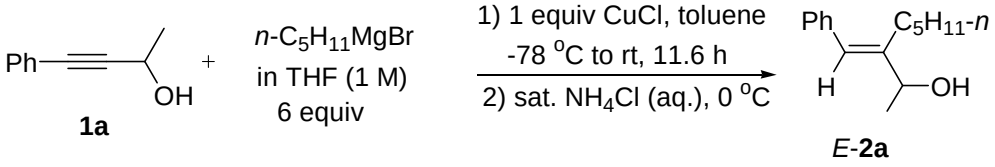
reaction mixture was worked up by filtration and washing with ether. Evaporation and purification by flash chromatography on silica gel (eluent: petroleum ether/ether = from 60/1 to 20/1) afforded (*S*)-**1a** (1.6780 g, 42%): ee > 99% (HPLC conditions: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, 1 mL/min, λ = 230 nm, tr 10.121 min (major), 8.978 min (minor), $[\alpha]^{23}_{D}$ = -45.4 ^{o} (*c* = 1.06, Et_2O)) and (*R*)-4-Phenyl-3-butyn-2-ol acetate (2.7696 g, 54%): ee = 71% (ee value was determined after its conversion to the corresponding alcohol), $[\alpha]^{20}_{D}$ = +145.8 ^{o} (*c* = 1.03, $CHCl_3$). (*S*)-**1a**: Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.39 (m, 2 H), 7.34-7.27 (m, 3 H), 4.76 (q, *J* = 6.6 Hz, 1 H), 2.16 (bs, 1 H), 1.56 (d, *J* = 6.6 Hz, 3 H). (*S*)-**1a** was prepared by a different method in 98% ee, $[\alpha]^{25}_{D}$ = -44.8 ^{o} (*c* = 1.0, Et_2O).[7]

3. General Procedure for the CuCl-Mediated Carbometallation of Propargylic Alcohols with Grignard Reagents Followed by Protonolysis

To a solution of CuCl (1.0 mmol, 1 equiv) and propargylic alcohol (1 mmol) in toluene (1.5 mL) under a nitrogen atmosphere was added the corresponding Grignard reagent (6 equiv, 6 mmol) dropwise at -78 ^{o}C in 15 min, which was followed by warming up to rt naturally. After complete conversion of the starting material as monitored by TLC, the reaction mixture was quenched with an aqueous solution of saturated NH_4Cl at 0 ^{o}C, and extracted with Et_2O. The combined organic layer was washed with 5 % HCl, sat. $NaHCO_3$ (aq.), brine, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the NMR yield and ratio were determined by using 1,3,5-trimethylbenzene as the internal standard (35 μL, 0.25 mmol). Chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40/1~2/1) of the crude product

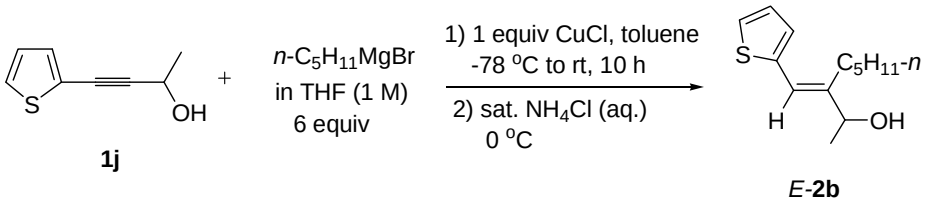
afforded the desired product.

(1) 3-(*n*-Pentyl)-4-phenyl-3(*E*)-buten-2-ol (*E*-2a)



The reaction of **1a** (0.1477 g, 1.0 mmol), CuCl (0.1005 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, and a solution of *n*-$C_5H_{11}MgBr$ in THF (1 M, 6 mL, 6 mmol, 6 equiv) afforded *E*-**2a** (0.1984 g, 90%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.38 (m, 2 H), 7.27-7.18 (m, 3 H), 6.56 (s, 1 H), 4.42 (q, *J* = 6.4 Hz, 1 H), 2.42-2.32 (m, 1 H), 2.22-2.10 (m, 1 H), 1.65-1.55 (m, 1 H), 1.55-1.43 (m, 2 H), 1.39 (d, *J* = 6.6 Hz, 3 H), 1.37-1.23 (m, 4 H), 0.91-0.83 (m, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.8, 137.7, 128.5, 128.1, 126.3, 124.0, 71.7, 32.2, 28.8, 28.4, 22.5, 22.3, 14.0; IR (neat, cm^{-1}) 3357, 3056, 3024, 2957, 2929, 2868, 1649, 1599, 1493, 1464, 1368, 1284, 1165, 1114, 1071; MS (m/z) 200 ((M^+-H_2O), 10.73), 129 (100); Elemental analysis calcd for $C_{15}H_{22}O$: C, 82.52, H, 10.16; Found: C, 82.86, H, 10.03.

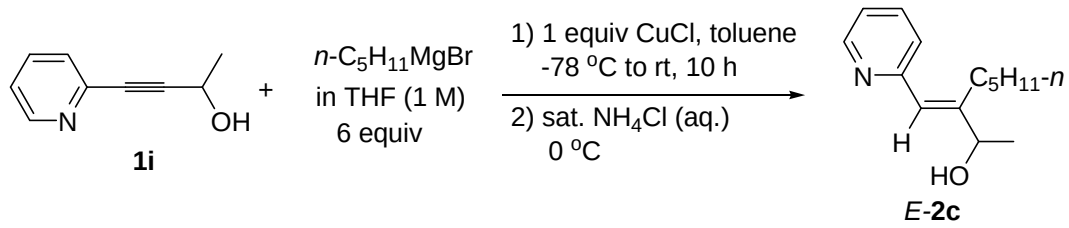
(2) 3-(*n*-Pentyl)-4-(2-thienyl)-3(*E*)-buten-2-ol (*E*-2b)



The reaction of **1j** (0.1530 g, 1.0 mmol), CuCl (0.0991 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, and a solution of *n*-$C_5H_{11}MgBr$ in THF (6 mL, 1 M, 6 mmol, 6 equiv) afforded *E*-**2b** (0.1881 g, 83%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.22 (m, 1 H), 7.02-6.95 (m, 2 H), 6.67 (s, 1 H), 4.38 (q, *J* = 6.3 Hz, 1 H), 2.54-2.42 (m, 1 H), 2.34-2.22 (m, 1 H), 1.70 (bs, 1 H), 1.60-1.47 (m, 2 H), 1.45-1.32 (m, 7 H), 0.91 (t, *J* =

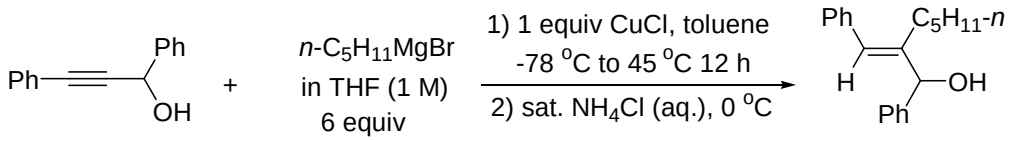
7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.1, 140.2, 127.2, 126.7, 124.9, 117.4, 72.4, 32.5, 29.3, 28.4, 22.5, 22.4, 14.1; IR (neat, cm^{-1}) 3357, 2956, 2931, 2869, 1637, 1508, 1466, 1367, 1319, 1282, 1214, 1156, 1103, 1059, 1007; MS (m/z) 224 (M^+, 28.70), 153 (100); Elemental analysis calcd for $C_{13}H_{20}OS$: C, 69.59, H, 8.98; Found: C, 69.54, H, 8.96.

(3) 3-(*n*-Pentyl)-4-(2-pyridyl)-3(*E*)-buten-2-ol (*E*-2c)



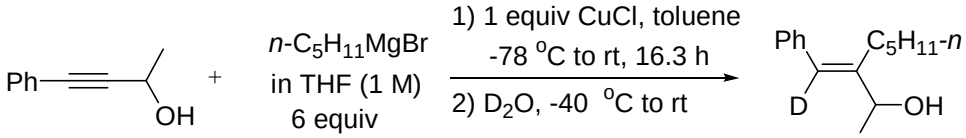
The reaction of **1i** (0.1471 g, 1.0 mmol), CuCl (0.0993 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, and a solution of *n*-C_5H_{11}MgBr in THF (6 mL, 1 M, 6 mmol, 6 equiv) afforded *E*-**2c** (0.1720 g, 78%). The organic layer was washed with brine. *E*-**2c**: Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59-5.55 (m, 1 H), 7.62 (td, *J* = 7.8 and *J* = 2.1 Hz, 1 H), 7.21 (d, *J* = 8.1 Hz, 1 H), 7.08 (ddd, *J* = 7.5, 5.0 and 1.2 Hz, 1 H), 6.60 (s, 1 H), 4.42 (q, *J* = 2.8 Hz, 1 H), 2.75-2.64 (m, 1 H), 2.40-2.28 (m, 1 H), 2.08 (bs, 1 H), 1.54-1.44 (m, 2 H), 1.40 (d, *J* = 6.3 Hz, 3 H), 1.34-1.22 (m, 4 H), 0.86 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 156.9, 151.7, 149.1, 135.9, 123.8, 123.0, 120.9, 71.7, 32.2, 28.7, 28.6, 22.5, 22.3, 14.0; IR (neat, cm^{-1}) 3379, 2957, 2929, 2868, 1648, 1586, 1563, 1468, 1429, 1367, 1291, 1152, 1118, 1059; MS (m/z) 219 (M^+, 7.65), 158 (100); HRMS calcd for $C_{14}H_{21}NONa$ (M^++Na): 242.1515; found: 242.1510.

(4) 2-(*n*-Pentyl)-1,3-diphenyl-3(*E*)-propen-2-ol (*E*-2d)



The reaction of **1c** (0.2092 g, 1.0 mmol), CuCl (0.1002 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, and a solution of *n*-C_5H_{11}MgBr in THF (6 mL, 1 M, 6 mmol, 6 equiv) afforded *E*-**2d** (0.1273 g, 45%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.40 (m, 2 H), 7.38-7.25 (m, 7 H), 7.25-7.17 (m, 1 H), 6.77 (s, 1 H), 5.31 (s, 1 H), 2.34-2.20 (m, 1 H), 2.05 (bs, 1 H), 2.02-1.90 (m, 1 H), 1.45-1.28 (m, 2 H), 1.25-1.12 (m, 4 H), 0.84-0.76 (m, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.3, 142.3, 137.6, 128.7, 128.4, 128.2, 127.7, 126.8, 126.5, 125.6, 77.8, 32.0, 28.6, 28.5, 22.2, 13.9; IR (neat, cm^{-1}) 3396, 3026, 2955, 2929, 2859, 1654, 1599, 1576, 1493, 1450, 1378, 1232, 1187, 1073, 1030; MS (m/z) 280 (M^+, 6.55), 209 (100); Elemental analysis calcd for $C_{20}H_{24}O$: C, 85.67, H, 8.63; Found: C, 85.75, H, 8.62.

4. Synthesis of 4-deutero-3-(*n*-pentyl)-4-phenyl-3(*E*)-buten-2-ol (*E*-5a)



Following the procedure for the CuCl-mediated carbometallation of propargylic alcohols with Grignard reagents described above, the reaction was conducted using **1a** (0.1488 g, 1.0 mmol), CuCl (0.0998 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, and a solution of *n*-C_5H_{11}MgBr in THF (6 mL, 1 M, 6 mmol, 6 equiv). After complete conversion of the starting material as monitored by TLC, the reaction mixture was quenched with D_2O (0.5 mL) at -40 °C and warmed up to rt to afford *E*-**5a** (0.1961 g,

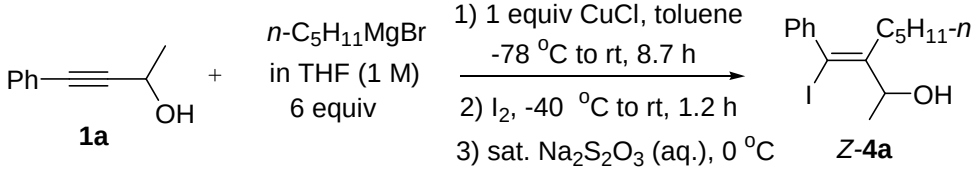
88%, D incorporation: 99%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.29 (m, 2 H), 7.27-7.17 (m, 3 H), 6.55 (s, 0.01 H), 4.41 (q, *J* = 6.4 Hz, 1 H), 2.42-2.30 (m, 1 H), 2.22-2.10 (m, 1 H), 1.77 (bs, 1 H), 1.56-1.42 (m, 2 H), 1.38 (d, *J* = 6.6 Hz, 3 H), 1.34-1.22 (m, 4 H), 0.90-0.83 (m, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.7, 137.6, 128.5, 128.1, 126.3, 71.7, 32.2, 28.8, 28.4, 22.5, 22.3, 14.0; IR (neat, cm^{-1}) 3363, 3056, 3021, 2957, 2929, 2868, 1639, 1597, 1493, 1464, 1370, 1285, 1114, 1063; MS (m/z) 219 (M^+, 3.22), 148 (100); HRMS calcd for $C_{15}H_{21}DO$ (M^+): 219.1733, found 219.1730.

5. General Procedure for the CuCl-Mediated Carbometallation of Propargylic Alcohols with Grignard Reagents Followed by Iodination

Following the procedure for the CuCl-mediated carbometallation of propargylic alcohols with Grignard reagents described above, the reaction was conducted using propargylic alcohol (1 mmol), CuCl (1.0 mmol, 1 equiv), 1.5 mL of toluene, and a solution of Grignard reagent in THF (6 equiv, 6 mmol). After complete conversion of the starting material as monitored by TLC, the reaction mixture was quenched by the dropwise addition of a solution of I_2 (6 mmol, 6 equiv) in 5 mL of THF at -40 ^{o}C, followed by warming up to rt naturally for 1 h, treatment with an aqueous solution of saturated $Na_2S_2O_3$ at 0 ^{o}C, and extraction with Et_2O. The combined organic layer was washed with 5 % HCl, sat. $NaHCO_3$ (aq.), brine, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the NMR yield and ratio were determined by using 1,3,5-trimethylbenzene as the internal standard (35 μL, 0.25 mmol). Chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1~10/1) of the crude product

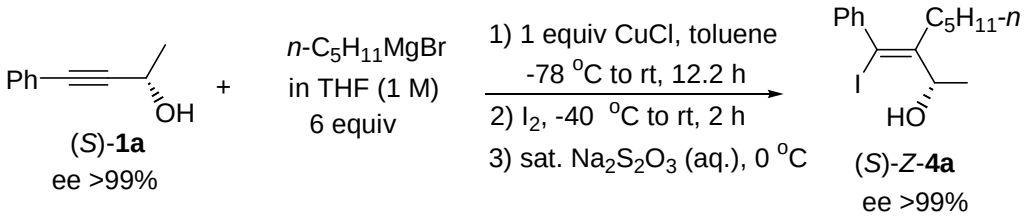
afforded the desired product.

(1) 4-Iodo-3-(*n*-pentyl)-4-phenyl-3(*Z*)-buten-2-ol (*Z*-4a)



The reaction of **1a** (0.1469 g, 1.0 mmol), CuCl (0.1007 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of *n*-$C_5H_{11}MgBr$ in THF (6 mL, 1 M, 6 mmol, 6 equiv), and a solution of I_2 (1.5243 g, 6.0 mmol, 6 equiv) in THF (5 mL) afforded *Z*-**4a** (0.2878 g, 83%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.28 (m, 2 H), 7.28-7.15 (m, 3 H), 4.97-4.87 (m, 1 H), 2.21-1.99 (m, 2 H), 1.93 (bs, 1 H), 1.40 (d, *J* = 6.3 Hz, 3 H), 1.36-1.20 (m, 2 H), 1.15-0.99 (m, 4 H), 0.74 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.3, 144.5, 128.2, 128.1, 127.6, 96.0, 77.0, 31.8, 29.8, 28.8, 22.0, 21.2, 13.8; IR (neat, cm^{-1}) 3363, 2956, 2928, 2865, 1620, 1592, 1486, 1458, 1442, 1367, 1285, 1222, 1175, 1104, 1060; MS (m/z) 344 (M^+, 0.50), 327 ($(M-H_2O)^+$, 22.04), 117 (100); HRMS calcd for $C_{15}H_{21}OI$ (M^+): 344.0637, found: 344.0642.

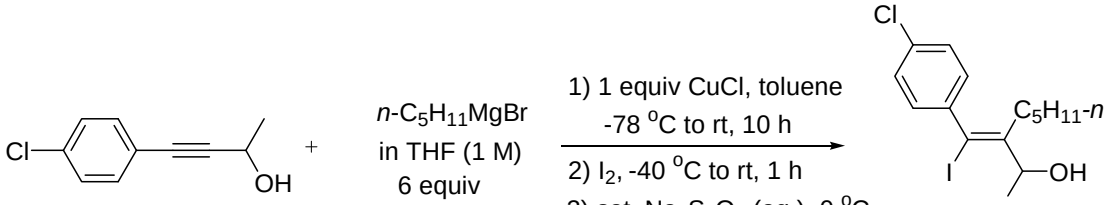
(2) (*S*)-4-Iodo-3-(*n*-pentyl)-4-phenyl-3(*Z*)-buten-2-ol ((*S*)-*Z*-4a)



The reaction of (*S*)-(–)-**1a** (0.1474 g, 1.0 mmol, ee > 99%), CuCl (0.0991 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of *n*-$C_5H_{11}MgBr$ in THF (6 mL, 1 M, 6 mmol, 6 equiv), and a solution of I_2 (1.4864 g, 5.9 mmol, 5.9 equiv) in THF (5 mL) afforded (*S*)-*Z*-**4a** (0.2541 g, 73 %): ee > 99% (HPLC conditions: Chiralcel AS-H,

n-hexane/*i*-PrOH = 95/5, 0.5 mL/min, λ = 230 nm, tr 9.474 min (major), 10.582 min (minor), $[\alpha]^{20}_{D}$ = +3.4 ^{o} (*c* = 1.02, $CHCl_3$)). Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.29 (m, 2 H), 7.27-7.17 (m, 3 H), 4.92 (qd, *J* = 6.4 and *J* = 3.0 Hz, 1 H), 2.21-1.99 (m, 2 H), 1.96-1.84 (m, 1 H), 1.44-1.24 (m, 5 H), 1.15-0.98 (m, 4 H), 0.74 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.3, 144.4, 128.1, 128.0, 127.5, 95.9, 76.9, 31.8, 29.7, 28.7, 21.9, 21.2, 13.8; IR (neat, cm^{-1}) 3355, 2956, 2928, 2869, 1612, 1592, 1487, 1458, 1442, 1367, 1286, 1222, 1104, 1060; MS (m/z) 344 (M^+, 3.33), 117 (100); HRMS calcd for $C_{15}H_{21}OI$ (M^+): 344.0637, found: 344.0645.

(3) 4-(*p*-Chlorophenyl)-4-iodo-3-(*n*-pentyl)-3(*Z*)-buten-2-ol (*Z*-4b)

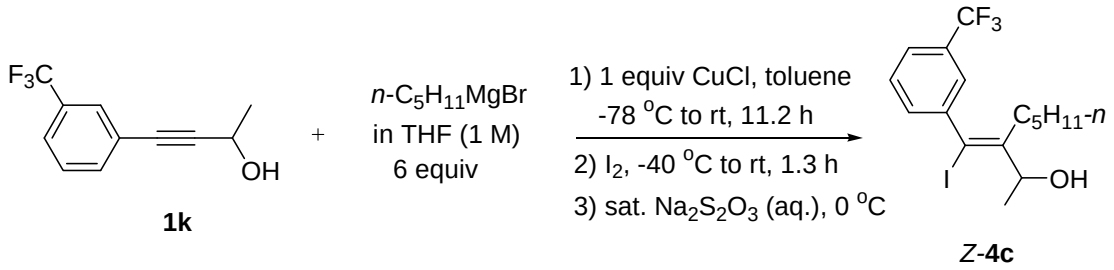


1h *Z*-**4b**

The reaction of **1h** (0.1801 g, 1.0 mmol), CuCl (0.1001 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of *n*-C_5H_{11}MgBr in THF (6 mL, 1 M, 6 mmol, 6 equiv), and a solution of I_2 (1.5261 g, 6.0 mmol, 6 equiv) in THF (5 mL) afforded *Z*-**4b** (0.2930 g, 78%): Solid: m.p. 70.5-71.0 ^{o}C (hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.26 (m, 2 H), 7.17-7.10 (m, 2 H), 4.89 (q, *J* = 6.6 Hz, 1 H), 2.20-1.98 (m, 2 H), 1.94 (bs, 1 H), 1.42-1.22 (m, 5 H), 1.18-1.00 (m, 4 H), 0.77 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.2, 142.9, 133.3, 129.5, 128.5, 94.1, 76.9, 31.8, 29.8, 28.9, 22.0, 21.2, 13.8; IR (KBr, cm^{-1}) 3363, 2956, 2929, 2869, 1587, 1486, 1465, 1395, 1367, 1221, 1088, 1060, 1015; MS (m/z) 380 (M^+(^{37}Cl), 0.73), 378 (M^+(^{35}Cl), 2.49), 125 (100); Elemental analysis calcd for $C_{15}H_{20}OClI$: C, 47.58, H, 5.32; Found:

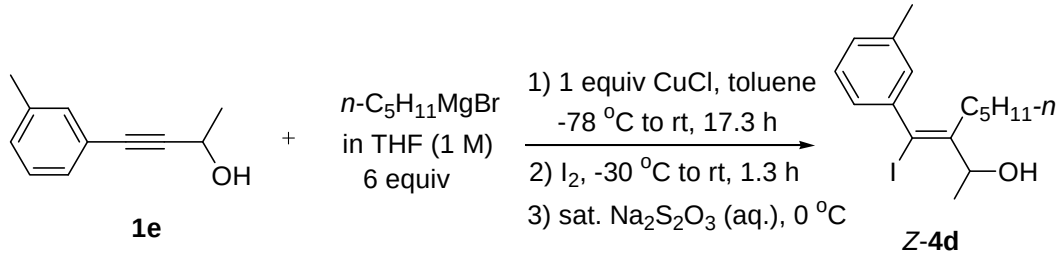
C, 47.59, H, 5.32.

(4) 4-Iodo-3-(*n*-pentyl)-4-(*m*-trifluoromethylphenyl)-3(*Z*)-buten-2-ol (*Z*-4c)



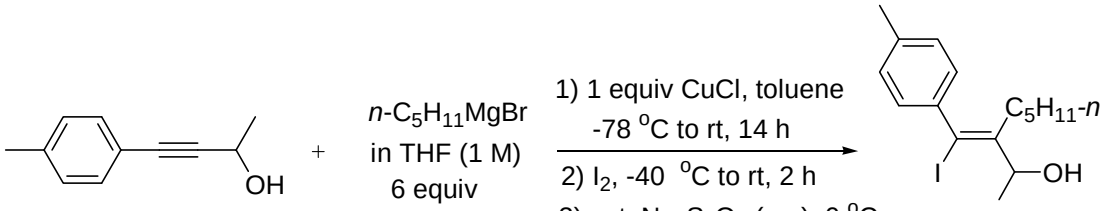
The reaction of **1k** (0.2080 g, 0.97 mmol), CuCl (0.0992 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of *n*-$C_5H_{11}MgBr$ in THF (6 mL, 1 M, 6 mmol, 6 equiv), and a solution of I_2 (1.5324 g, 6.0 mmol, 6 equiv) in THF (5 mL) afforded *Z*-**4c** (0.3020 g, 75%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.43 (m, 3 H), 7.42-7.37 (m, 1 H), 4.92 (qd, *J* = 6.5 and 3.3 Hz, 1 H), 2.18-1.98 (m, 2 H), 1.92 (d, *J* = 3.3 Hz, 1 H), 1.41 (d, *J* = 6.6 Hz, 3 H), 1.38-1.23 (m, 2 H), 1.15-1.00 (m, 4 H), 0.74 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.0, 145.1, 131.6, 130.6 (q, *J* = 32.1 Hz, 1 C), 128.8, 125.0 (q, *J* = 3.9 Hz, 1 C), 124.3 (q, *J* = 3.8 Hz, 1 C), 123.8, (q, *J* = 271 Hz, 1 C), 93.1, 76.8, 31.8, 29.8, 28.9, 21.9, 21.3, 13.7; ^{19}F NMR ($CDCl_3$, 282 MHz) -62.8; IR (neat, cm^{-1}) 3373, 2959, 2931, 2871, 1604, 1589, 1484, 1461, 1432, 1368, 1329, 1310, 1210, 1167, 1131, 1093, 1072, 1001; MS (m/z) 412 (M^+, 1.47), 185 (100), HRMS calcd for $C_{16}H_{20}F_3OI$ (M^+): 412.0511, found: 412.0503.

(5) 4-Iodo-4-(*m*-methylphenyl)-3-(*n*-pentyl)-3(*Z*)-buten-2-ol (*Z*-4d)



The reaction of **1e** (0.1628 g, 1.0 mmol), CuCl (0.0966 g, 0.98 mmol, 1 equiv), 1.5 mL of toluene, a solution of *n*-$C_5H_{11}MgBr$ in THF (6 mL, 1 M, 6 mmol, 6 equiv), and a solution of I_2 (1.5294 g, 6.0 mmol, 6 equiv) in THF (5 mL) afforded *Z*-**4d** (0.1795 g, 49%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24-7.17 (m, 1 H), 7.06-6.97 (m, 3 H), 4.91 (q, *J* = 6.6 Hz, 1 H), 2.33 (s, 3 H), 2.20-1.98 (m, 2 H), 1.92-1.84 (m, 1 H), 1.42-1.25 (m, 5 H), 1.18-0.98 (m, 4 H), 0.75 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.1, 144.4, 137.8, 128.6, 128.4, 128.1, 125.1, 96.4, 77.0, 31.8, 29.8, 28.8, 22.0, 21.4, 21.2, 13.8; IR (neat, cm^{-1}) 3383, 2956, 2928, 2860, 1597, 1581, 1481, 1456, 1377, 1367, 1252, 1217, 1183, 1159, 1104, 1059, 1000; MS (m/z) 358 (M^+, 7.08), 231 (100); Elemental analysis calcd for $C_{16}H_{23}IO$: C, 53.64, H, 6.47; Found: C, 53.67, H, 6.47.

(6) 4-Iodo-4-(*p*-methylphenyl)-3-(*n*-pentyl)-3(*Z*)-buten-2-ol (*Z*-4e)

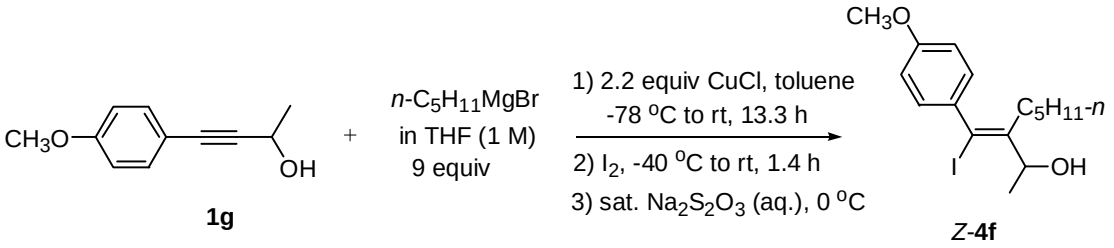


1f *Z*-**4e**

The reaction of **1f** (0.0806 g, 0.50 mmol), CuCl (0.0498 g, 0.50 mmol, 1 equiv), 0.75 mL of toluene, a solution of *n*-$C_5H_{11}MgBr$ in THF (3 mL, 1 M, 3 mmol, 6 equiv), and I_2 (0.7532 g, 3.0 mmol, 6 equiv) afforded *Z*-**4e** (0.1191 g, 66%): Solid: m.p. 52.1-52.8 °C (hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.07 (m, 4 H), 4.90 (q, *J* = 6.5 Hz, 1 H), 2.34 (s, 3 H), 2.21-1.99 (m, 2 H), 1.93 (bs, 1 H), 1.43-1.25 (m, 5 H), 1.18-1.00 (m, 4 H), 0.75 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.1, 141.8, 137.3, 128.9, 128.0, 96.5, 77.1, 31.8, 29.8, 28.8, 22.0, 21.2,

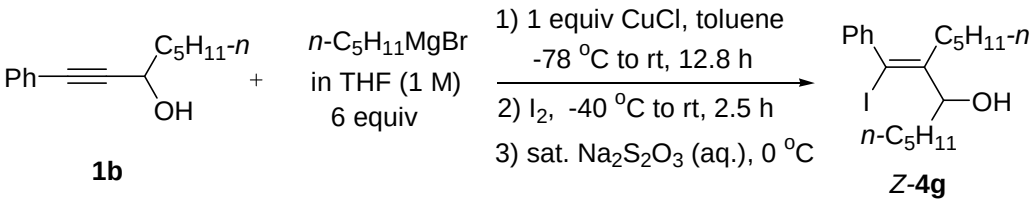
13.8; IR (KBr, cm^{-1}) 3373, 3022, 2956, 2927, 2869, 1603, 1570, 1506, 1456, 1404, 1367, 1262, 1224, 1180, 1106, 1059, 1021; MS (m/z) 358 (M^+, 0.50), 341 ((M^+-OH), 1.83), 105 (100); HRMS calcd for $C_{16}H_{23}OI$ (M^+): 358.0794, found: 358.0780.

(7) 4-Iodo-4-(*p*-methoxyphenyl)-3-(*n*-pentyl)-3(*Z*)-buten-2-ol (*Z*-4f)



The reaction of **1g** (0.1591 g, 0.90 mmol), CuCl (0.1966 g, 2.0 mmol, 2.2 equiv), 1.5 mL of toluene, a solution of *n*-$C_5H_{11}MgBr$ in THF (8 mL, 1 M, 8 mmol, 9 equiv), and a solution of I_2 (2.0013 g, 7.9 mmol, 9 equiv) in THF (7 mL) afforded *Z*-**4f** (0.1907 g, 56%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16-7.11 (m, 2 H), 6.87-6.81 (m, 2 H), 4.90 (q, *J* = 6.5 Hz, 1 H), 3.81 (s, 3 H), 2.22-2.00 (m, 3 H), 1.42-1.25 (m, 5 H), 1.18-1.00 (m, 4 H), 0.76 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.6, 149.2, 137.1, 129.4, 113.5, 96.4, 77.1, 55.2, 31.8, 29.8, 28.8, 22.0, 21.1, 13.8; IR (neat, cm^{-1}) 3440, 2956, 2869, 1602, 1574, 1505, 1464, 1441, 1366, 1288, 1247, 1173, 1106, 1034; MS (m/z) 374 (M^+, 0.80), 121 (100); Elemental analysis calcd for $C_{16}H_{23}O_2I$: C, 51.35, H, 6.19; Found: C, 51.31, H, 6.22.

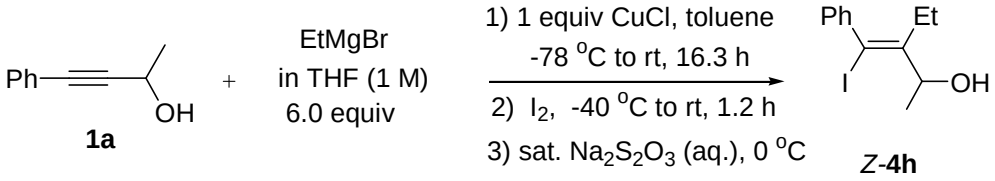
(8) 1-Iodo-2-(*n*-pentyl)-1-phenyl-1(*Z*)-octen-3-ol (*Z*-4g)



The reaction of **1b** (0.2106 g, 1.0 mmol), CuCl (0.1038 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of *n*-$C_5H_{11}MgBr$ in THF (6 mL, 1 M, 6 mmol, 6 equiv),

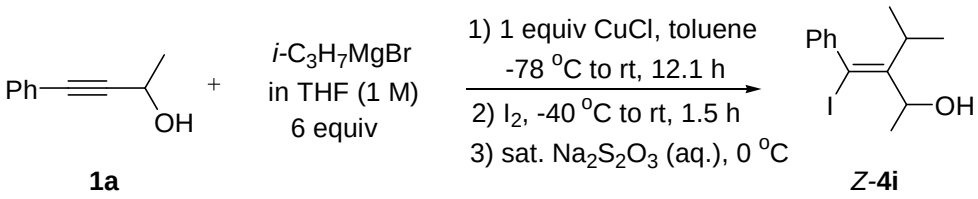
and a solution of I_2 (1.5382 g, 6.1 mmol, 6 equiv) in THF (5 mL) afforded *Z*-**4g** (0.1304 g, 31%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2 H), 7.25-7.17 (m, 3 H), 4.72 (t, *J* = 6.6 Hz, 1 H), 2.20-1.96 (m, 3 H), 1.71-1.50 (m, 2 H), 1.48-1.20 (m, 8 H), 1.14-0.97 (m, 4 H), 0.96-0.88 (m, 3 H), 0.72 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.9, 144.6, 128.1, 128.0, 127.5, 96.7, 80.9, 35.3, 31.8, 31.7, 29.7, 28.9, 25.7, 22.6, 21.9, 14.1, 13.8; IR (neat, cm^{-1}) 3396, 3057, 2955, 2929, 2859, 1620, 1592, 1487, 1462, 1378, 1304, 1215, 1116, 1029; MS (m/z) 400 (M^+, 0.49), 91 (100); Elemental analysis calcd for $C_{19}H_{29}OI$: C, 57.00, H, 7.30; Found: C, 57.00, H, 7.32.

(9) 3-Ethyl-4-iodo-4-phenyl-3(*Z*)-buten-2-ol (*Z*-4h)



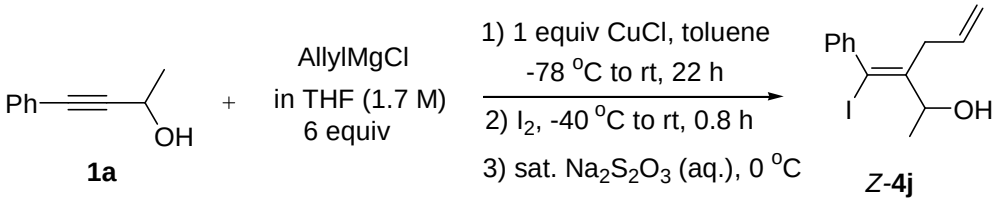
The reaction of **1a** (0.1440 g, 0.99 mmol), CuCl (0.1008 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of EtMgBr in THF (6 mL, 1 M, 6 mmol, 6 equiv), and a solution of I_2 (1.5325 g, 6.0 mmol, 6 equiv) in THF (5 mL) afforded *Z*-**4h** (0.2452 g, 82%): Solid: m.p. 100.2-101.0 °C (hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.29 (m, 2 H), 7.27-7.18 (m, 3 H), 4.98-4.89 (m, 1 H), 2.36-2.07 (m, 3 H), 1.41 (d, *J* = 6.6 Hz, 3 H), 0.92 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.3, 144.4, 128.2, 128.0, 127.5, 95.9, 77.0, 21.9, 21.2, 15.0; IR (KBr, cm^{-1}) 3318, 3052, 2976, 2967, 2930, 2870, 1615, 1576, 1485, 1440, 1373, 1367, 1342, 1288, 1218, 1184, 1103, 1072, 1052, 1015; MS (m/z) 302 (M^+, 2.81), 131 (100); Elemental analysis calcd for $C_{12}H_{15}OI$: C, 47.70, H, 5.00; Found: C, 47.73, H, 5.01.

(10) 4-Iodo-3-isopropyl-4-phenyl-3(*Z*)-buten-2-ol (*Z*-4i)



The reaction of **1a** (0.1426 g, 0.98 mmol), CuCl (0.1041 g, 1.1 mmol, 1 equiv), 1.5 mL of toluene, a solution of *i*-C_3H_7MgBr in THF (6 mL, 1 M, 6 mmol, 6 equiv), and a solution of I_2 (1.5432 g, 6.1 mmol, 6 equiv) in THF (5 mL) afforded *Z*-**4i** (0.2575 g, 83%): Solid: m.p. 88.7-89.2 °C (hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.28 (m, 2 H), 7.27-7.15 (m, 3 H), 4.84 (q, *J* = 6.6 Hz, 1 H), 2.88-2.73 (m, 1 H), 2.28 (bs, 1 H), 1.54 (d, *J* = 6.9 Hz, 3 H), 1.05 (d, *J* = 6.9 Hz, 3 H), 0.96 (d, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.8, 145.4, 128.2, 127.9, 127.5, 94.6, 74.3, 31.8, 21.9, 21.8, 21.3; IR (KBr, cm^{-1}) 3361, 2982, 2963, 2932, 2872, 1616, 1587, 1574, 1477, 1458, 1440, 1365, 1227, 1161, 1109, 1057; MS (m/z) 316 (M^+, 0.80), 145 (100); Elemental analysis calcd for $C_{13}H_{17}IO$: C, 49.38, H, 5.42; Found: C, 49.40, H, 5.41.

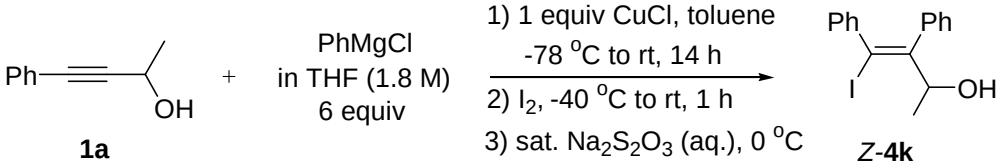
(11) 3-Allyl-4-iodo-4-phenyl-3(*Z*)-buten-2-ol (*Z*-4j)



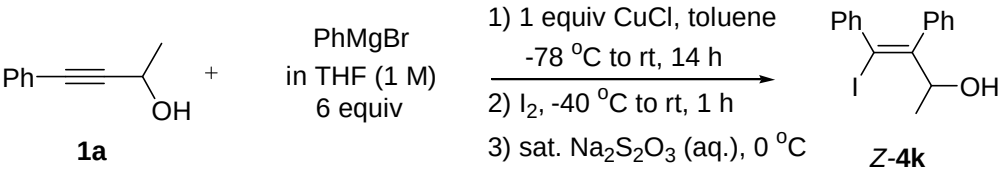
The reaction of **1a** (0.2973 g, 2.0 mmol), CuCl (0.2038 g, 2.1 mmol, 1 equiv), 3 mL of toluene, a solution of CH_2=$CHCH_2MgCl$ in THF (7 mL, 1.7 M, 12 mmol, 6 equiv), and a solution of I_2 (3.0215 g, 11.9 mmol, 6 equiv) in THF (10 mL) afforded *Z*-**4j** (0.3160 g, 49%): Solid: m.p. 47.7-49.9 °C (hexane/ethyl acetate); ^{1}H NMR (300

MHz, $CDCl_3$) δ 7.36-7.28 (m, 2 H), 7.27-7.18 (m, 3 H), 5.83-5.68 (m, 1 H), 5.01-4.88 (m, 3 H), 2.93 (qdt, *J* = 13.1, 6.3, and 1.7 Hz, 2 H), 2.23 (d, *J* = 3.3 Hz, 1 H), 1.39 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.2, 144.1, 137.0, 128.2, 128.0, 127.8, 116.1, 97.0, 77.0, 32.8, 21.2; IR (KBr, cm^{-1}) 3396, 3077, 3058, 2975, 2927, 1637, 1588, 1573, 1487, 1442, 1411, 1367, 1285, 1219, 1177, 1103, 1061, 1029, 1000; MS (m/z) 314 (M^+, 5.86), 128 (100); Elemental analysis calcd for $C_{13}H_{15}OI$: C, 49.70, H, 4.81; Found: C, 49.66, H, 4.83.

(12) 4-Iodo-3,4-diphenyl-3-buten-2(*Z*)-ol (*Z*-4k)

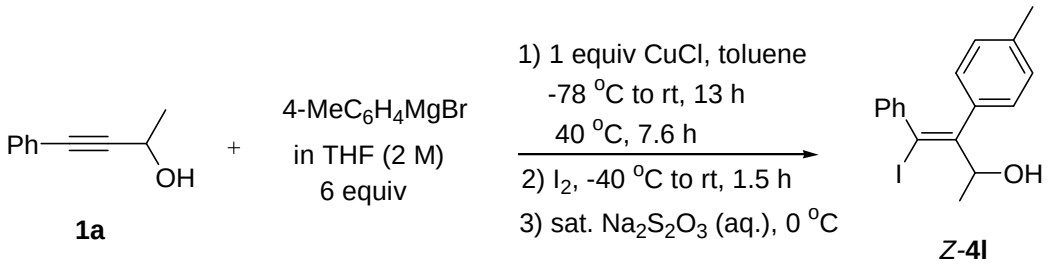


The reaction of **1a** (0.1467 g, 1.0 mmol), CuCl (0.1032 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of PhMgCl in THF (3.4 mL, 1.8 M, 6 mmol, 6 equiv), and a solution of I_2 (1.5237 g, 6.0 mmol, 6 equiv) in THF (5 mL) afforded *Z*-**4k** (0.2435 g, 69%): Solid: m.p. 99.1-100.8 °C (hexane/ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$) δ 7.19-7.10 (m, 3 H), 7.09-6.95 (m, 7 H), 5.18-5.08 (m, 1 H), 1.69 (bs, 1 H), 1.31 (d, *J* = 6.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.2, 143.7, 135.7, 130.0, 129.1, 127.7, 127.5, 127.2, 127.0, 100.7, 76.6, 21.4; IR (KBr, cm^{-1}) 3339, 2977, 1597, 1574, 1486, 1440, 1365, 1283, 1111, 1057; MS (m/z) 350 (M^+, 5.03), 179 (100); Elemental analysis calcd for $C_{16}H_{15}OI$: C, 54.88, H, 4.32; Found: C, 54.87, H, 4.32.



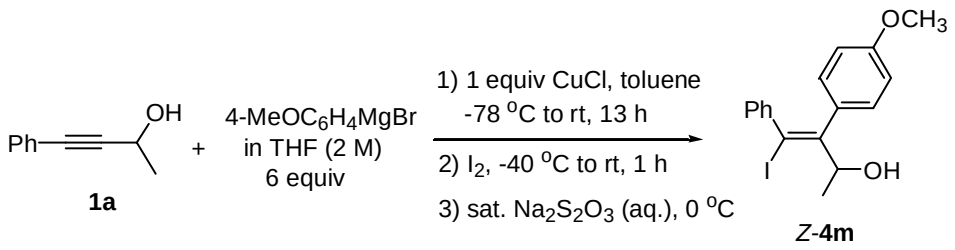
The reaction of **1a** (0.1449 g, 1 mmol), CuCl (0.1013 g, 1 mmol, 1 equiv), 1.5 mL of toluene, a solution of PhMgBr in THF (6 mL, 1 M, 6 mmol, 6 equiv), and a solution of I_2 (1.5245 g, 6 mmol, 6 equiv) in THF (5 mL) afforded *Z*-**4k** (0.2174 g, 63%). The data of the compound are the same as those desribed in the previous experiment.

(13) 4-Iodo-3-(*p*-methylphenyl)-4-phenyl-3(*Z*)-buten-2-ol (*Z*-4l)



The reaction of **1a** (0.1473 g, 1.0 mmol), CuCl (0.0993 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of 4-MeC_6H_4MgBr in THF (3 mL, 2 M, 6 mmol, 6 equiv), and a solution of I_2 (1.5244 g, 6.0 mmol, 6 equiv) in THF (5 mL) afforded *Z*-**4l** (0.3030 g, 83%): Solid: m.p. 112.0-112.4 °C (hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09-6.87 (m, 9 H), 5.16-5.05 (m, 1 H), 2.20 (s, 3 H), 1.88-1.74 (m, 1 H), 1.30 (d, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.1, 143.9, 136.7, 132.6, 129.8, 129.2, 128.5, 127.5, 127.1, 100.4, 76.6, 21.4, 21.1; IR (KBr, cm^{-1}) 3406, 3078, 3024, 2973, 2922, 2866, 1609, 1590, 1576, 1509, 1487, 1442, 1403, 1367, 1329, 1263, 1200, 1184, 1113, 1055; MS (m/z) 365 ((M^++1), 1.97), 364 (M^+, 9.73), 193 (100); Elemental analysis calcd for $C_{17}H_{17}OI$: C, 56.06, H, 4.70; Found: C, 56.10, H, 4.70.

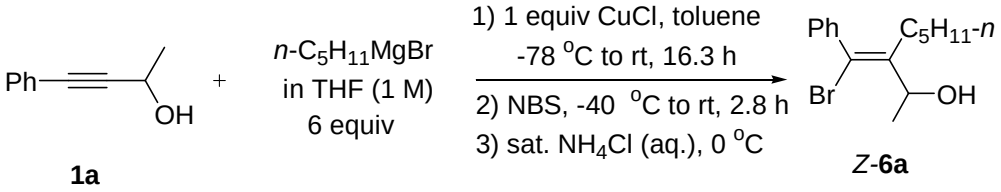
(14) 4-Iodo-3-(*p*-methoxyphenyl)-4-phenyl-3(*Z*)-buten-2-ol (*Z*-4m)



1a *Z*-**4m**

The reaction of **1a** (0.1442 g, 1.0 mmol), CuCl (0.1017 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of 4-$MeOC_6H_4MgBr$ in THF (6 mL, 1 M, 6 mmol, 6 equiv), and a solution of I_2 (1.5241 g, 6.0 mmol, 6 equiv) in THF (5 mL) afforded *Z*-**4m** (0.2732 g, 73%): Solid: m.p. 97.1-98.3 °C (hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11-6.99 (m, 5 H), 6.96-6.90 (m, 2 H), 6.70-6.64 (m, 2 H), 5.16-5.06 (m, 1 H), 3.70 (s, 3 H), 1.78 (d, *J* = 6.0 Hz, 1 H), 1.30 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.5, 149.8, 144.0, 131.2, 129.3, 127.8, 127.6, 127.2, 113.3, 100.7, 76.6, 55.1, 21.5; IR (KBr, cm^{-1}) 3424, 2971, 2930, 2835, 1605, 1573, 1508, 1488, 1463, 1441, 1366, 1287, 1246, 1177, 1112, 1056, 1031; MS (m/z) 380 (M^+, 16.08), 209 (100); Elemental analysis calcd for $C_{17}H_{17}O_2I$: C, 53.70, H, 4.51; Found: C, 53.77, H, 4.56.

6. Synthesis of 4-Bromo-3-(*n*-pentyl)-4-phenyl-3(*Z*)-buten-2-ol (*Z*-6a)



1a *Z*-**6a**

Following the procedure for the CuCl-mediated carbometallation of propargylic alcohols with Grignard reagents described above, the reaction was conducted using **1a** (0.1408 g, 0.96 mmol), CuCl (0.0998 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, and a solution of *n*-$C_5H_{11}MgBr$ in THF (6 mL, 1 M, 6 mmol, 6 equiv). After complete conversion of the starting material as monitored by TLC, the reaction mixture was

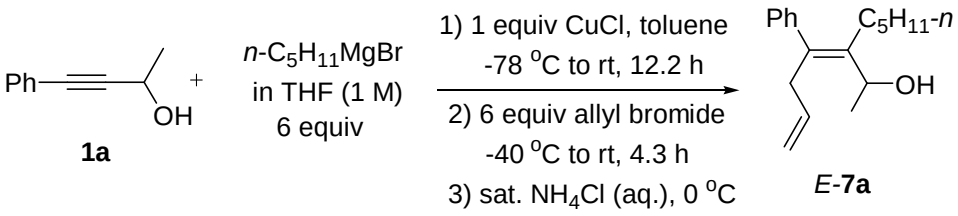
quenched with NBS (1.1170 g, 6.3 mmol, 6.3 equiv) at -40 ^{o}C to afford *Z*-**6a** (0.1545 g, 54%): Solid: m.p. 47.9-48.8 ^{o}C (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.24 (m, 5 H), 5.09 (q, *J* = 6.5 Hz, 1 H), 2.18-1.98 (m, 2 H), 1.91 (bs, 1 H), 1.45-1.30 (m, 5 H), 1.17-1.01 (m, 4 H), 0.76 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.0, 140.8, 128.6, 128.2, 127.9, 117.8, 71.3, 31.8, 29.5, 29.3, 22.0, 21.2, 13.8; IR (KBr, cm^{-1}) 3386, 3058, 2957, 2929, 2868, 1632, 1593, 1488, 1443, 1368, 1263, 1230, 1104, 1061, 1029; MS (m/z) 298 (M^{+}(^{81}Br), 0.83), 296 (M^{+}(^{79}Br), 0.90), 217 (100); Elemental analysis calcd for $C_{15}H_{21}BrO$: C, 60.61, H, 7.12; Found: C, 60.57, H, 7.15.

7. General Procedure for the CuCl-Mediated Carbometallation of Propargylic Alcohols with Grignard Reagents Followed by Allylation

Following the procedure for the CuCl-mediated carbometallation of propargylic alcohols with Grignard reagents described above, the reaction was conducted using propargylic alcohol (1 mmol), CuCl (1.0 mmol, 1 equiv), 1.5 mL of toluene, and a solution of Grignard reagent in THF (6 equiv, 6 mmol). After complete conversion of the starting material as monitored by TLC, the reaction mixture was quenched by the dropwise addition of a solution of allyl bromide in 2 mL of THF at -40 ^{o}C, followed by warming up to rt naturally. The resulting mixture was treated with an aqueous solution of saturated NH_4Cl at 0 ^{o}C, and extracted with Et_2O. The combined organic layer was washed with 5 % HCl, sat. $NaHCO_3$ (aq.), brine, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the NMR yield and ratio were determined by using 1,3,5-trimethylbenzene as the internal standard (35 μL, 0.25 mmol). Chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40/1~10/1) of

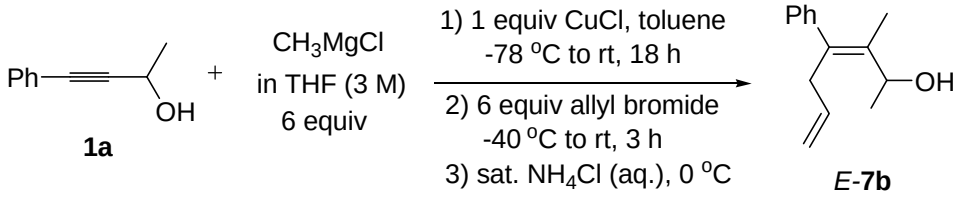
the crude product afforded the desired product.

(1) 3-(*n*-Pentyl)-4-phenylhepta-3(*E*),6-dien-2-ol (*E*-7a)



The reaction of **1a** (0.1499 g, 1.0 mmol), CuCl (0.1041 g, 1.1 mmol, 1 equiv), 1.5 mL of toluene, a solution of *n*-$C_5H_{11}MgBr$ in THF (6 mL, 1 M, 6 mmol, 6 equiv), and a solution of allyl bromide (0.54 mL, *d* = 1.398 g/mL, 0.7549 g, 6.2 mmol, 6.2 equiv) in THF (2 mL) afforded *E*-**7a** (0.2250 g, 85%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2 H), 7.26-7.18 (m, 1 H), 7.11-7.07 (m, 2 H), 5.82-5.67 (m, 1 H), 5.05-4.89 (m, 3 H), 3.15 (qdt, *J* = 12.9, 6.3, and 1.5 Hz, 2 H), 2.02-1.85 (m, 2 H), 1.59 (bs, 1 H), 1.38 (d, *J* = 6.6 Hz, 3 H), 1.35-1.19 (m, 2 H), 1.15-0.96 (m, 4 H), 0.74 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.4, 140.3, 136.0, 135.5, 128.4, 127.9, 126.2, 115.2, 67.6, 38.7, 32.2, 30.3, 28.4, 22.1, 22.0, 13.9; IR (neat, cm^{-1}) 3382, 3077, 3057, 3019, 2956, 2929, 2870, 1636, 1599, 1491, 1456, 1441, 1368, 1283, 1106, 1177, 1072, 1056; MS (m/z) 258 (M^+, 1.22), 130 (100); HRMS calcd for $C_{18}H_{26}ONa$ (M^+ + Na): 281.1876, Found: 281.1870.

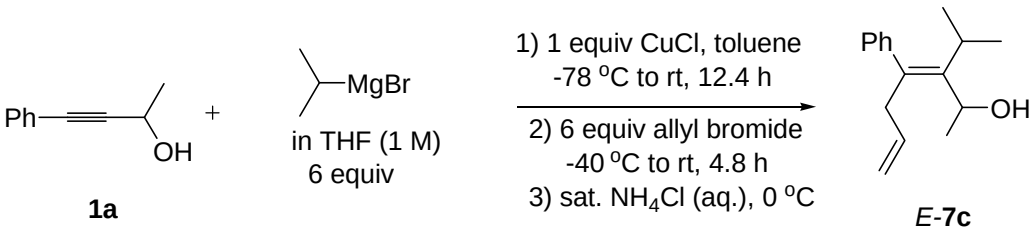
(2) 3-Methyl-4-phenylhepta-3(*E*),6-dien-2-ol (*E*-7b)



The reaction of **1a** (0.1475 g, 1.0 mmol), CuCl (0.0984 g, 0.99 mmol, 1 equiv), 1.5 mL of toluene, a solution of CH_3MgCl in THF (2 mL, 3 M, 6 mmol, 6 equiv), and

a solution of allyl bromide (0.54 mL, d = 1.398 g/mL, 0.7549 g, 6.2 mmol, 6.2 equiv) in THF (2 mL) afforded *E*-**7b** (0.1858 g, 91%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2 H), 7.25-7.18 (m, 1 H), 7.13-7.08 (m, 2 H), 5.82-5.68 (m, 1 H), 5.05-4.91 (m, 3 H), 3.26-3.06 (m, 2 H), 1.75 (bs, 1 H), 1.58 (s, 3 H), 1.34 (d, J = 6.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.3, 136.1, 135.6, 133.9, 128.5, 127.9, 126.2, 115.1, 66.7, 38.2, 21.3, 13.1; IR (neat, cm^{-1}) 3364, 3077, 2975, 2926, 2862, 1636, 1601, 1492, 1442, 1405, 1376, 1290, 1091; MS (m/z) 202 (M^+, 1.64), 130 (100); Elemental analysis calcd for $C_{14}H_{18}O$: C, 83.12, H, 8.97; Found: C, 83.10, H, 8.95.

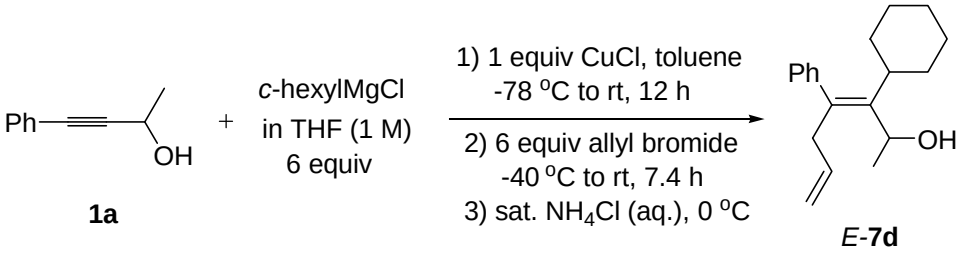
(3) 3-Isopropyl-4-phenylhepta-3(*E*),6-dien-2-ol (*E*-7c)



The reaction of **1a** (0.1465 g, 1.0 mmol), CuCl (0.0978 g, 0.99 mmol, 1 equiv), 1.5 mL of toluene, a solution of *i*-C_3H_7MgBr in THF (6 mL, 1 M, 6 mmol, 6 equiv), and a solution of allyl bromide (0.7364 g, 6 mmol, 6 equiv) in THF (2 mL) afforded *E*-**7c** (0.1887 g, 82%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.26 (m, 2 H), 7.25-7.18 (m, 1 H), 7.08-7.03 (m, 2 H), 5.76-5.61 (m, 1 H), 4.99-4.87 (m, 2 H), 4.65 (q, J = 6.8 Hz, 1 H), 3.47-3.33 (m, 2 H), 2.48 (h, J = 6.9 Hz, 1 H), 1.82 (bs, 1 H), 1.52 (dd, J = 6.6 and 0.6 Hz, 3 H), 0.98 (dd, J = 6.9 and 0.3 Hz, 3 H), 0.87 (d, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.9, 143.2, 136.4, 136.3, 128.4, 127.8, 126.0, 115.4, 66.0, 39.4, 31.1, 23.7, 21.5, 21.2; IR (neat, cm^{-1}) 3439, 3076, 2962, 2930, 2870, 1634, 1597, 1574, 1490, 1462, 1441, 1412, 1370, 1259, 1111, 1071, 1049; MS (m/z)

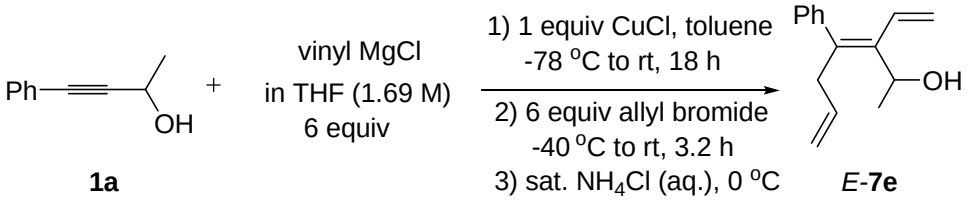
230 (M^+, 0.27), 212 ((M^+-H_2O), 5.75), 187 (100); Elemental analysis calcd for $C_{16}H_{22}O$: C, 83.43, H, 9.63; Found: C, 83.50, H, 9.63.

(4) 3-Cyclohexyl-4-phenylhepta-3(*E*),6-dien-2-ol (*E*-7d)



The reaction of **1a** (0.1446 g, 1.0 mmol), CuCl (0.1033 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of *c*-$C_6H_{11}MgCl$ in THF (6 mL, 1 M, 6 mmol, 6 equiv), and a solution of allyl bromide (0.7336 g, 6.1 mmol, 6.1 equiv) in THF (2 mL) afforded *E*-**7d** (0.2033 g, 76%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.19 (m, 3 H), 7.06-7.01 (m, 2 H), 5.68 (ddt, *J* = 17.3, 10.2, and 4.8 Hz, 1 H), 4.99-4.88 (m, 2 H), 4.66 (q, *J* = 6.7 Hz, 1 H), 3.39 (qdt, *J* = 13.2, 6.6, and 1.5 Hz, 2 H), 2.08 (tt, *J* = 11.8 and 3.5 Hz, 1 H), 1.65-1.57 (m, 4 H), 1.55-1.38 (m, 7 H), 1.05-0.95 (m, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.8, 143.3, 136.8, 136.4, 128.4, 127.8, 126.1, 115.4, 67.0, 42.3, 39.5, 31.6, 31.4, 26.4, 26.3, 25.9, 23.5; IR (neat, cm^{-1}) 3416, 3076, 2927, 2851, 1635, 1597, 1490, 1448, 1369, 1257, 1094, 1071; MS (m/z) 270 (M^+, 0.92), 187 (100); Elemental analysis calcd for $C_{19}H_{26}O$: C, 84.39, H, 9.69; Found: C, 84.44, H, 9.65.

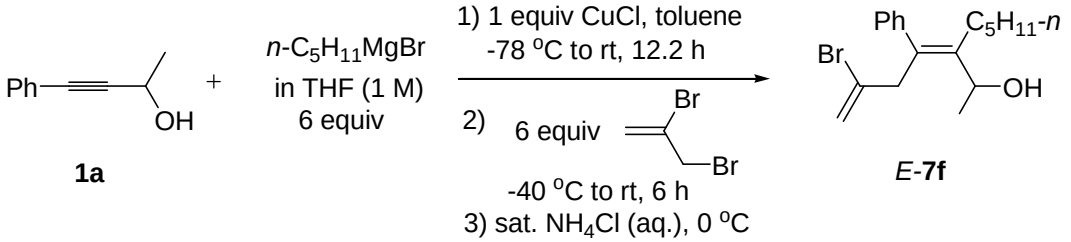
(5) 4-Phenyl-3-vinylhepta-3(*E*),6-dien-2-ol (*E*-7e)



The reaction of **1a** (0.1465 g, 1.0 mmol), CuCl (0.0999 g, 1.0 mmol, 1 equiv),

1.5 mL of toluene, a solution of CH_2=CHMgCl in THF (3.55 mL, 1.69 M, 6 mmol, 6 equiv), and a solution of allyl bromide (0.54 mL, *d* = 1.398 g/mL, 0.7549 g, 6.2 mmol, 6.2 equiv) in THF (2 mL) afforded *E*-**7e** (0.1652 g, 77%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.20 (m, 3 H), 7.16-7.11 (m, 2 H), 6.11 (dd, *J* = 18 and 11.7 Hz, 1 H), 5.82-5.68 (m, 1 H), 5.45 (dd, *J* = 18 and 1.8 Hz, 1 H), 5.14-4.95 (m, 4 H), 3.38 (ddt, *J* = 15.3, 6.0, and 1.7 Hz, 1 H), 3.23 (ddt, *J* = 15.0, 6.0, and 1.7 Hz, 1 H), 2.04 (bs, 1 H), 1.52 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.6, 139.2, 137.8, 135.4, 133.7, 128.9, 127.9, 126.6, 115.7, 115.6, 67.0, 39.1, 22.2; IR (neat, cm^{-1}) 3405, 3078, 2976, 2930, 1635, 1620, 1490, 1442, 1414, 1369, 1280, 1074; MS (m/z) 214 (M^+, 2.26), 129 (100); Elemental analysis calcd for $C_{15}H_{18}O$: C, 84.07, H, 8.47; Found: C, 84.02, H, 8.50.

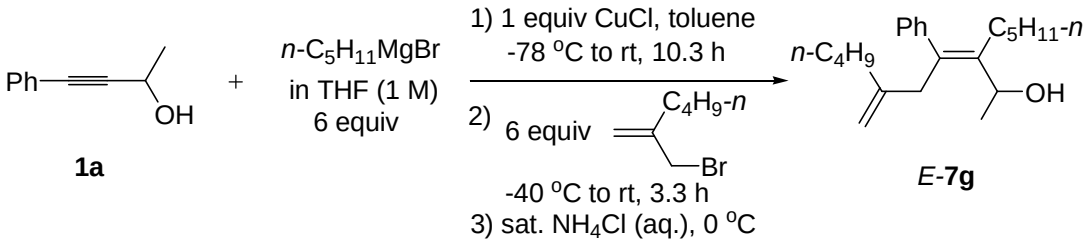
(6) 6-Bromo-3-(*n*-pentyl)-4-phenylhepta-3(*E*),6-dien-2-ol (*E*-7f)



The reaction of **1a** (0.1455 g, 1.0 mmol), CuCl (0.0999 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of *n*-C_5H_{11}MgBr in THF (6 mL, 1 M, 6 mmol, 6 equiv), and a solution of 2-bromoallyl bromide (1.1931 g, 6.0 mmol, 6 equiv) in THF (2 mL) afforded *E*-**7f** (0.1612 g, 48%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.19 (m, 3 H), 7.14-7.08 (m, 2 H), 5.41 (d, *J* = 1.8 Hz, 1 H), 5.40 (d, *J* = 1.5 Hz, 1 H), 4.93 (q, *J* = 6.5 Hz, 1 H), 3.55 (s, 2 H), 2.05-1.92 (m, 2 H), 1.86 (bs, 1 H), 1.40 (d, *J* = 6.6 Hz, 3 H), 1.36-1.20 (m, 2 H), 1.15-0.97 (m, 4 H), 0.73 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR

($CDCl_3$, 75 MHz) δ 143.1, 141.8, 133.0, 131.4, 128.5, 127.9, 126.5, 118.2, 67.4, 45.7, 32.2, 30.0, 28.5, 22.0, 21.7, 13.8; IR (neat, cm^{-1}) 3419, 2956, 2929, 2870, 1626, 1599, 1576, 1491, 1465, 1441, 1377, 1262, 1106, 1056, 1023; MS (m/z) 338 (M^+(^{81}Br), 1.03), 336 (M^+(^{79}Br), 0.99), 129 (100); Elemental analysis calcd for $C_{18}H_{25}BrO$: C, 64.10, H, 7.47; Found: C, 64.16, H, 7.56.

(7) 6-(*n*-Butyl)-3-(*n*-pentyl)-4-phenylhepta-3(*E*),6-dien-2-ol



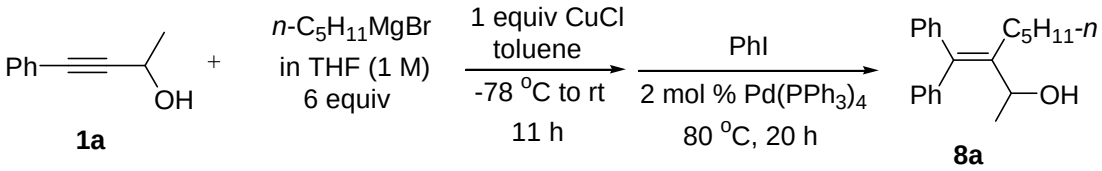
The reaction of **1a** (0.1439 g, 0.99 mmol), CuCl (0.1004 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of *n*-$C_5H_{11}MgBr$ in THF (6 mL, 1 M, 6 mmol, 6 equiv), and a solution of 2-(*n*-butyl)allyl bromide (0.9897 g, 6.1 mmol, 6.1 equiv) in THF (2 mL) afforded *E*-**7g** (0.2433 g, 79%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.24 (m, 2 H), 7.23-7.16 (m, 1 H), 7.14-7.09 (m, 2 H), 4.88-4.76 (m, 3 H), 3.15-3.00 (m, 2 H), 2.08-1.90 (m, 4 H), 1.52 (bs, 1 H), 1.40-1.20 (m, 9 H), 1.17-0.98 (m, 4 H), 0.85 (t, *J* = 7.2 Hz, 3 H), 0.74 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.9, 143.8, 141.1, 135.2, 128.4, 127.8, 126.1, 109.9, 67.8, 40.9, 36.5, 32.3, 30.4, 29.8, 28.1, 22.4, 22.1, 21.7, 13.93, 13.88; IR (neat, cm^{-1}) 3406, 2957, 2929, 2871, 1645, 1599, 1576, 1491, 1465, 1441, 1378, 1263, 1179, 1055; MS (m/z) 314 (M^+, 4.03), 243 (100); Elemental analysis calcd for $C_{22}H_{34}O$: C, 84.02, H, 10.90; Found: C, 84.07, H, 10.91.

8. General Procedure for the Pd-catalyzed Kumada-type Coupling Reaction

Following the procedure for the CuCl-mediated carbometallation of propargylic

alcohols with Grignard reagents described above, the reaction was conducted using propargylic alcohol (1 mmol), CuCl (1.0 mmol, 1 equiv), 1.5 mL of toluene, and a solution of Grignard reagent in THF (6 equiv, 6 mmol). After complete conversion of the starting material as monitored by TLC, $Pd(PPh_3)_4$ (2 mol %, 0.02 mmol) and a solution of aryl or vinyl iodide (6 equiv, 6 mmol) in THF (2 mL) were added sequentially at rt. The resulting mixture was then heated at 80 ^oC and monitored by TLC until the starting material disappeared. This mixture was then quenched with an aqueous solution of saturated NH_4Cl, and extracted with Et_2O (15 mL x 3). The combined organic layer was washed with 5 % HCl, sat. $NaHCO_3$ (aq.), brine, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the NMR yield and ratio were determined by using 1,3,5-trimethylbenzene as the internal standard (35 μL, 0.25 mmol). Chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1~10/1) of the crude product afforded the desired product.

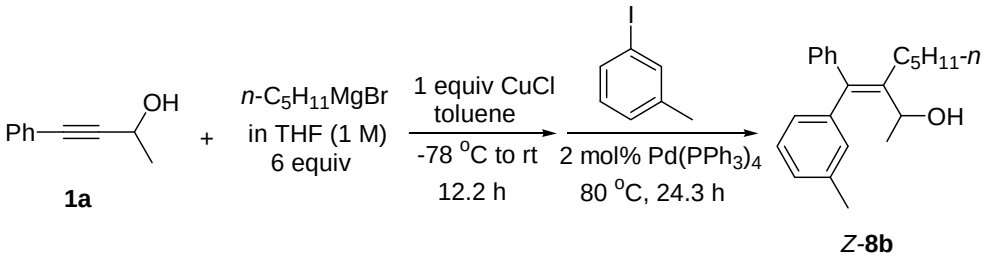
(1) 3-(*n*-Pentyl)-4,4-diphenyl-3-buten-2-ol (8a)



The reaction of **1a** (0.1458 g, 1.0 mmol), CuCl (0.0992 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of *n*-$C_5H_{11}MgBr$ in THF (6 mL, 1 M, 6 mmol, 6 equiv), $Pd(PPh_3)_4$ (0.0237 g, 0.02 mmol, 2 mol%), and PhI (1.2537 g, 6.2 mmol, 6 equiv)/ THF (2 mL) afforded **8a** (0.2204 g, 75%). According to ^1H NMR analysis of the crude reaction mixture before separation, product **8a** was formed in 80% yield together with 7% of the protonolysis product **2a**. **8a**: Liquid; ^1H NMR (300 MHz,

$CDCl_3$) δ 7.29-7.20 (m, 4 H), 7.19-7.10 (m, 6 H), 4.63 (q, J = 6.6 Hz, 1 H), 2.22-2.10 (m, 2 H), 1.77 (s, 1 H), 1.52-1.33 (m, 2 H), 1.30 (d, J = 6.6 Hz, 3 H), 1.18-1.03 (m, 4 H), 0.75 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.6, 142.2, 141.5, 139.9, 128.8, 128.7, 128.1, 128.0, 126.4, 126.3, 68.3, 32.2, 30.2, 27.3, 22.0, 21.9, 13.8; IR (neat, cm^{-1}) 3405, 3077, 3055, 3020, 2956, 2929, 2870, 1597, 1576, 1490, 1465, 1443, 1367, 1257, 1100, 1073, 1054, 1031, 1002; MS (m/z) 294 (M^+, 2.19), 167 (100); Elemental analysis calcd for $C_{21}H_{26}O$: C, 85.67, H, 8.90; Found: C, 85.66, H, 8.83.

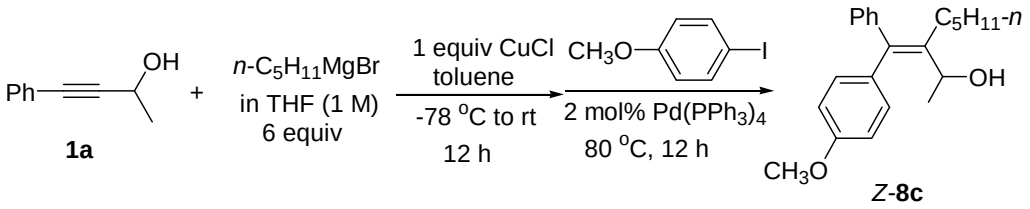
(2) 4-(*m*-Methylphenyl)-3-(*n*-pentyl)-4-phenyl-3(*Z*)-buten-2-ol (*Z*-8b)



The reaction of **1a** (0.1421 g, 0.97 mmol), CuCl (0.1004 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of *n*-$C_5H_{11}MgBr$ in THF (6 mL, 1 M, 6 mmol, 6 equiv), $Pd(PPh_3)_4$ (0.0343 g, 0.03 mmol, 3 mol%), and 3-iodotoluene (1.3033 g, 6.0 mmol, 6 equiv)/THF (2 mL) afforded *Z*-**8b** (0.2234 g, 75%). According to ^{1}H NMR analysis of the crude reaction mixture before separation, product *Z*-**8b** was formed in 77% yield together with 6% of the protonolysis product **2a**. *Z*-**8b**: Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.24 (m, 2 H), 7.22-7.14 (m, 4 H), 7.04-6.98 (m, 1 H), 6.97-6.92 (m, 2 H), 4.64 (q, J = 6.5 Hz, 1 H), 2.29 (s, 3 H), 2.20-2.13 (m, 2 H), 1.45-1.35 (m, 3 H), 1.31 (d, J = 6.6 Hz, 3 H), 1.19-1.05 (m, 4 H), 0.76 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.7, 142.3, 141.3, 140.3, 137.7, 129.4, 128.7, 128.1, 128.0, 127.3, 126.3, 125.9, 68.5, 32.3, 30.3, 27.4, 22.1, 22.0, 21.4, 13.9; IR (neat, cm^{-1}) 3418,

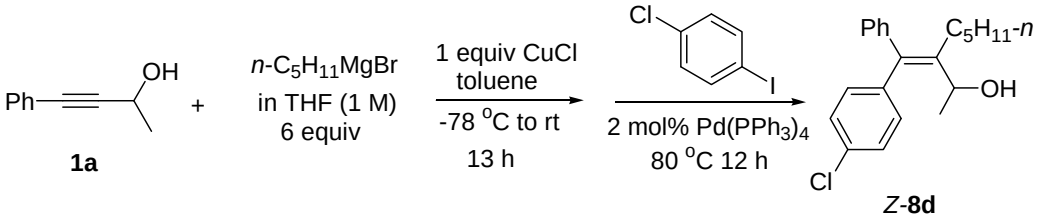
3054, 3020, 2956, 2928, 2868, 1599, 1581, 1490, 1461, 1443, 1377, 1258, 1098, 1054, 1004; MS (m/z) 308 (M^+, 2.05), 181 (100); HRMS calcd for $C_{22}H_{28}O$ (M^+): 308.2140, Found: 308.2141.

(3) 4-(*p*-Methoxyphenyl)-3-(*n*-pentyl)-4-phenyl-3(*Z*)-buten-2-ol (*Z*-8c)



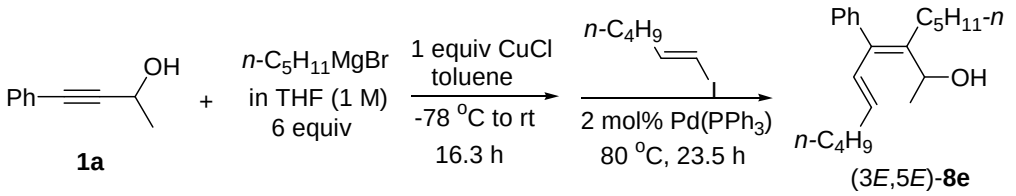
The reaction of **1a** (0.1467 g, 1.0 mmol), CuCl (0.1002 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of *n*-$C_5H_{11}MgBr$ in THF (6 mL, 1 M, 6 mmol, 6 equiv), $Pd(PPh_3)_4$ (0.0236 g, 0.02 mmol, 2 mol%), and 4-iodoanisole (1.3891 g, 5.9 mmol, 5.9 equiv)/THF (2 mL) afforded *Z*-**8c** (0.2412 g, 74%). According to ^1H NMR analysis of the crude reaction mixture before separation, product *Z*-**8c** was formed in 80% yield together with 9% of the protonolysis product **2a**. *Z*-**8c**: Liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.31-7.24 (m, 2 H), 7.21-7.13 (m, 3 H), 7.08-7.02 (m, 2 H), 6.84-6.78 (m, 2 H), 4.69 (q, *J* = 6.4 Hz, 1 H), 3.76 (s, 3 H), 2.24-2.08 (m, 2 H), 1.57-1.48 (m, 1 H), 1.47-1.25 (m, 5 H), 1.20-1.02 (m, 4 H), 0.76 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.2, 143.0, 141.2, 139.8, 134.7, 130.1, 128.8, 128.1, 126.3, 113.5, 68.5, 55.2, 32.3, 30.3, 27.5, 22.1, 22.0, 13.9; IR (neat, cm^{-1}) 3422, 3055, 2955, 2931, 2870, 1606, 1574, 1508, 1463, 1442, 1367, 1283, 1244, 1175, 1103, 1072, 1037; MS (m/z) 324 (M^+, 2.03), 197 (100); HRMS calcd for $C_{22}H_{28}O_2$ (M^+): 324.2089, Found: 324.2088.

(4) 4-(*p*-Chlorophenyl)-3-(*n*-pentyl)-4-phenyl-3(*Z*)-buten-2-ol (*Z*-8d)



The reaction of **1a** (0.1450 g, 1.0 mmol), CuCl (0.1012 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of *n*-C_5H_{11}MgBr in THF (6 mL, 1 M, 6 mmol, 6 equiv), $Pd(PPh_3)_4$ (0.0234 g, 0.02 mmol, 2 mol%), and 4-chloroiodotoluene (1.4257 g, 6.0 mmol, 6 equiv) in THF (2 mL) afforded *Z*-**8d** (0.2269 g, 69%). According to ^{1}H NMR analysis of the crude reaction mixture before separation, product *Z*-**8d** was formed in 71% yield together with 10% of the protonolysis product **2a**. *Z*-**8d**: Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.16 (m, 5 H), 7.16-7.05 (m, 4 H), 4.62 (q, *J* = 6.4 Hz, 1 H), 2.24-2.12 (m, 2 H), 1.46-1.30 (m, 6 H), 1.15-1.04 (m, 4 H), 0.76 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.24, 142.19, 140.7, 138.9, 132.4, 130.3, 128.8, 128.4, 128.2, 126.6, 68.4, 32.3, 30.2, 27.4, 22.11, 22.06, 13.9; IR (neat, cm^{-1}) 3405, 3056, 2956, 2929, 2868, 1596, 1488, 1464, 1443, 1395, 1376, 1259, 1192, 1090, 1055, 1015; MS (m/z) 330 (M^+(^{37}Cl), 0.37), 328 (M^+(^{35}Cl), 1.12), 201 (100); HRMS calcd for $C_{21}H_{25}{}^{35}ClO$ (M^+): 328.1594, Found: 328.1595.

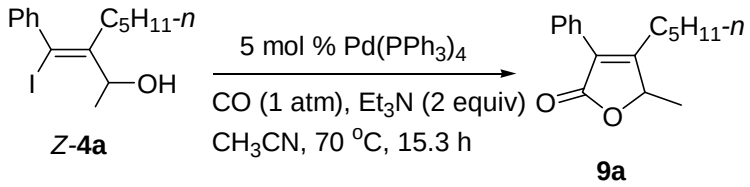
(5) 3-(*n*-Pentyl)-4-phenyl-3(*E*),5(*E*)-decadien-2-ol ((3*E*,5*E*)-8e)



The reaction of **1a** (0.1446, 0.99 mmol), CuCl (0.1032 g, 1.0 mmol, 1 equiv), 1.5 mL of toluene, a solution of *n*-C_5H_{11}MgBr in THF (6 mL, 1 M, 6 mmol, 6 equiv), $Pd(PPh_3)_4$ (0.0263 g, 0.02 mmol, 2 mol%), and 1(*E*)-hexenyl iodide (1.2556 g, 6.0

mmol, 6 equiv)/THF (2 mL) afforded (3*E*,5*E*)-**8e** (0.1431, 48%): Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) 7.37-7.20 (m, 3 H), 7.10-7.00 (m, 2 H), 6.71 (d, *J* = 15.3, 1 H), 5.12 (q, *J* = 6.6 Hz, 1 H), 5.05-4.94 (m, 1 H), 2.08-1.98 (m, 2 H), 1.92-1.80 (m, 2 H), 1.61 (bs, 1 H), 1.41 (d, *J* = 6.6 Hz, 3 H), 1.35-1.16 (m, 6 H), 1.12-0.95 (m, 4 H), 0.88-0.81 (m, 3 H), 0.73 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.8, 140.3, 137.1, 135.0, 129.6, 128.2, 127.8, 126.2, 67.3, 33.0, 32.2, 31.5, 30.3, 29.4, 22.2, 22.1, 13.90, 13.86; IR (neat, cm^{-1}) 3376, 3056, 3029, 2957, 2927, 2859, 1632, 1601, 1574, 1491, 1462, 1376, 1284, 1176, 1098, 1057, 1026; MS (m/z) 282 ((M^+-H_2O), 40.66), 169 (100); Elemental analysis calcd for $C_{21}H_{32}O$: C, 83.94, H, 10.73; Found: C, 83.84, H, 10.79.

9. Synthesis of 5-methyl-4-(*n*-pentyl)-3-phenyl-2(5*H*)-furanone (9a)



Z-**4a** **9a**

To a Schlenk tube were added $Pd(PPh_3)_4$ (0.0242 g, 0.02 mmol, 5 mol%), *Z*-**4a** (0.1372 g, 0.40 mmol), Et_3N (0.0828 g, 0.82 mmol, 2 equiv), and CH_3CN (4 mL) at rt. This mixture was degassed using greeze-pump-thaw cycles with CO and then heated at 70 °C. After complete conversion of the starting material as monitored by TLC, the reaction mixture was quenched by H_2O (5 mL) and extracted with Et_2O (20 mL x 3). The combined organic layer was washed with 5 % HCl (10 mL), sat. $NaHCO_3$ (aq.) (10 mL), brine (10 mL), and dried over anhydrous Na_2SO_4. Chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) of the crude product afforded **9a** (0.0656 g, 67%). Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47-7.32 (m, 5 H), 5.06 (q, *J*

= 6.7 Hz, 1 H), 2.77-2.65 (m, 1 H), 2.42-2.30 (m, 1 H), 1.60-1.40 (m, 5 H), 1.35-1.20 (m, 4 H), 0.91-0.82 (m, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.6, 166.1, 130.0, 128.8, 128.3, 128.2, 126.4, 77.9, 31.6, 27.4, 26.7, 22.1, 18.3, 13.8; IR (neat, cm^{-1}) 2954, 2931, 2866, 1752, 1656, 1601, 1493, 1446, 1376, 1322, 1150, 1100, 1062; MS (m/z) 244 (M^+, 58.66), 91 (100); Elemental analysis calcd for $C_{16}H_{20}O_2$: C, 78.65, H, 8.25; Found: C, 78.64, H, 8.26.

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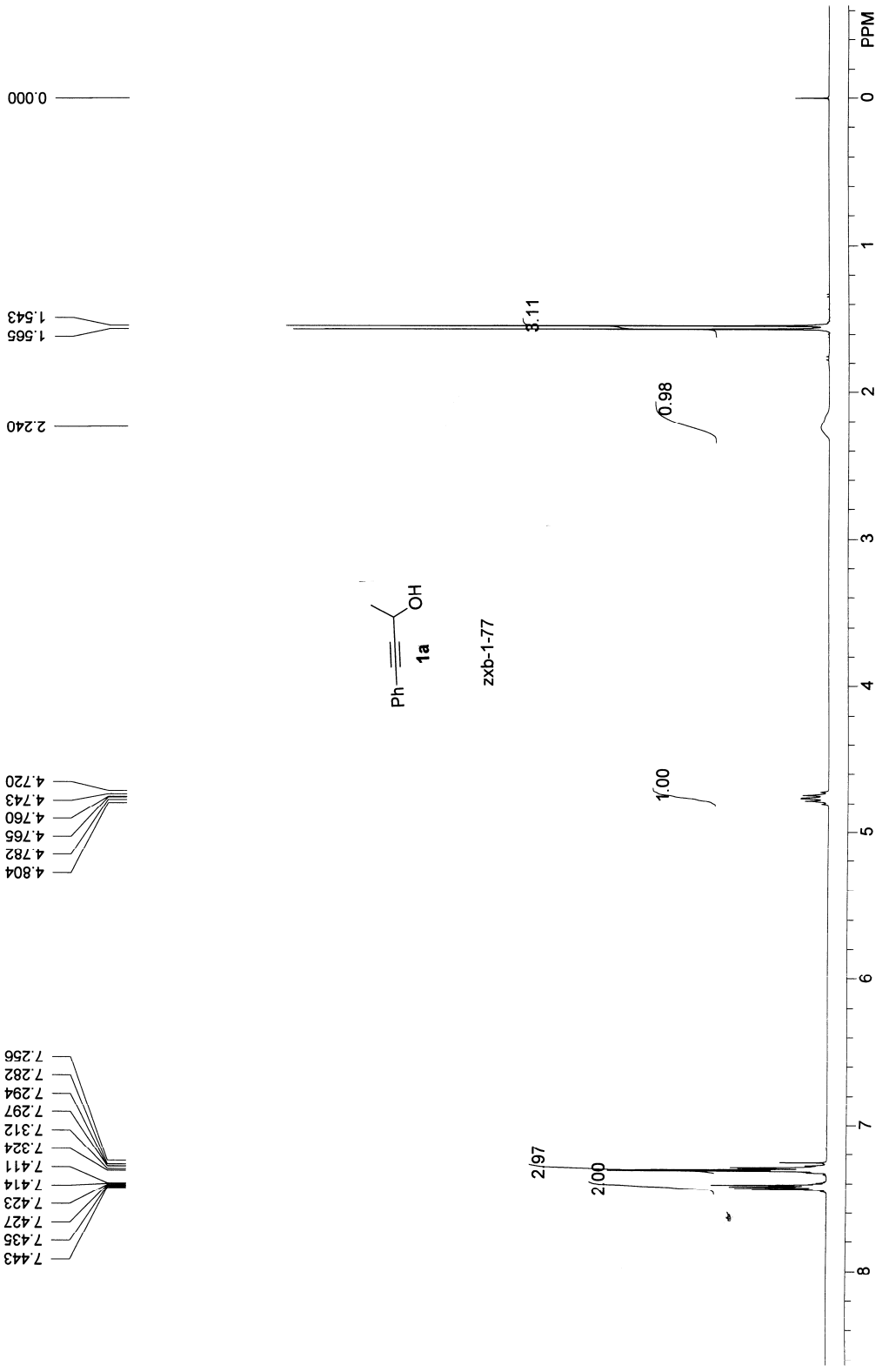
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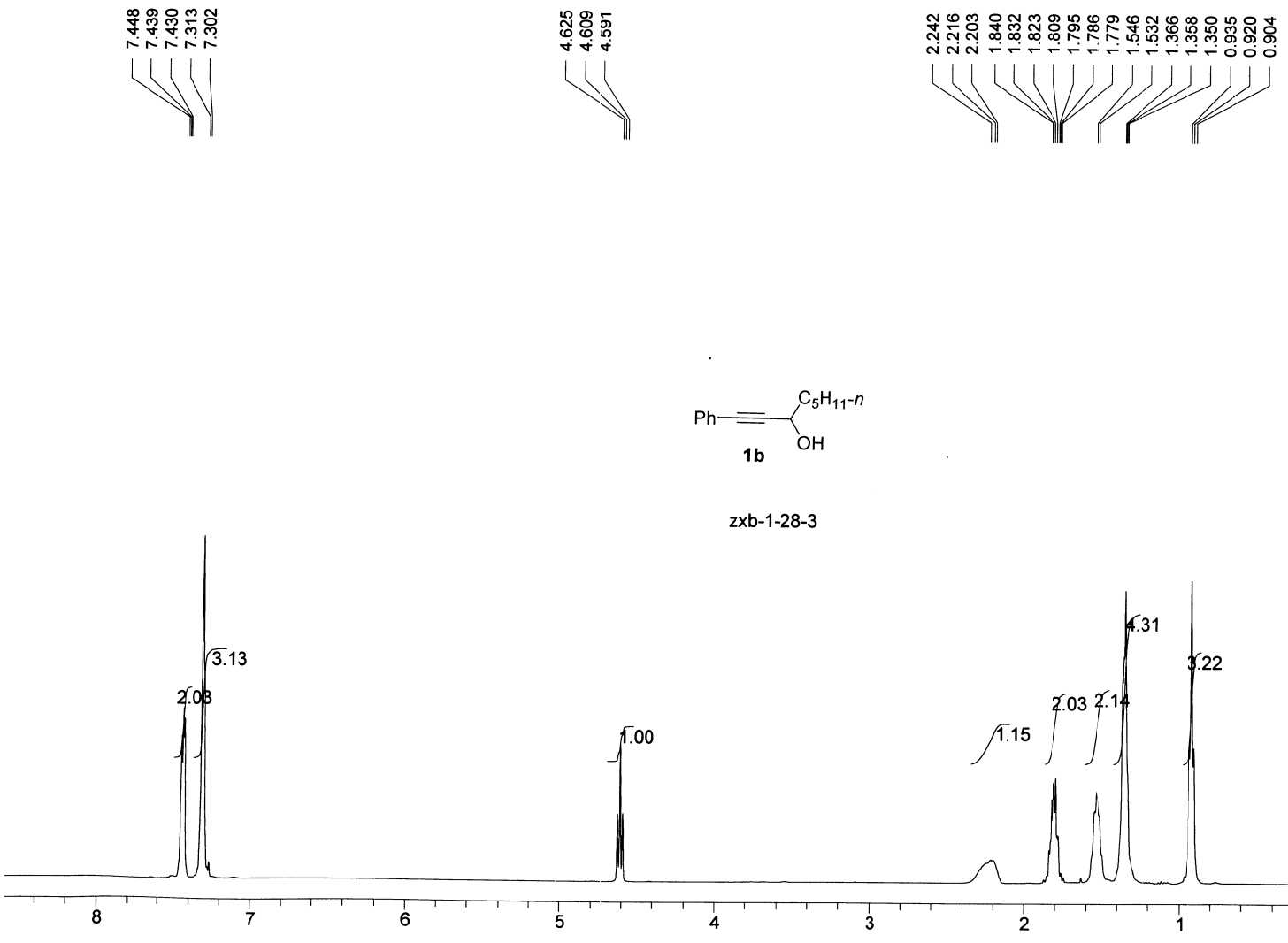
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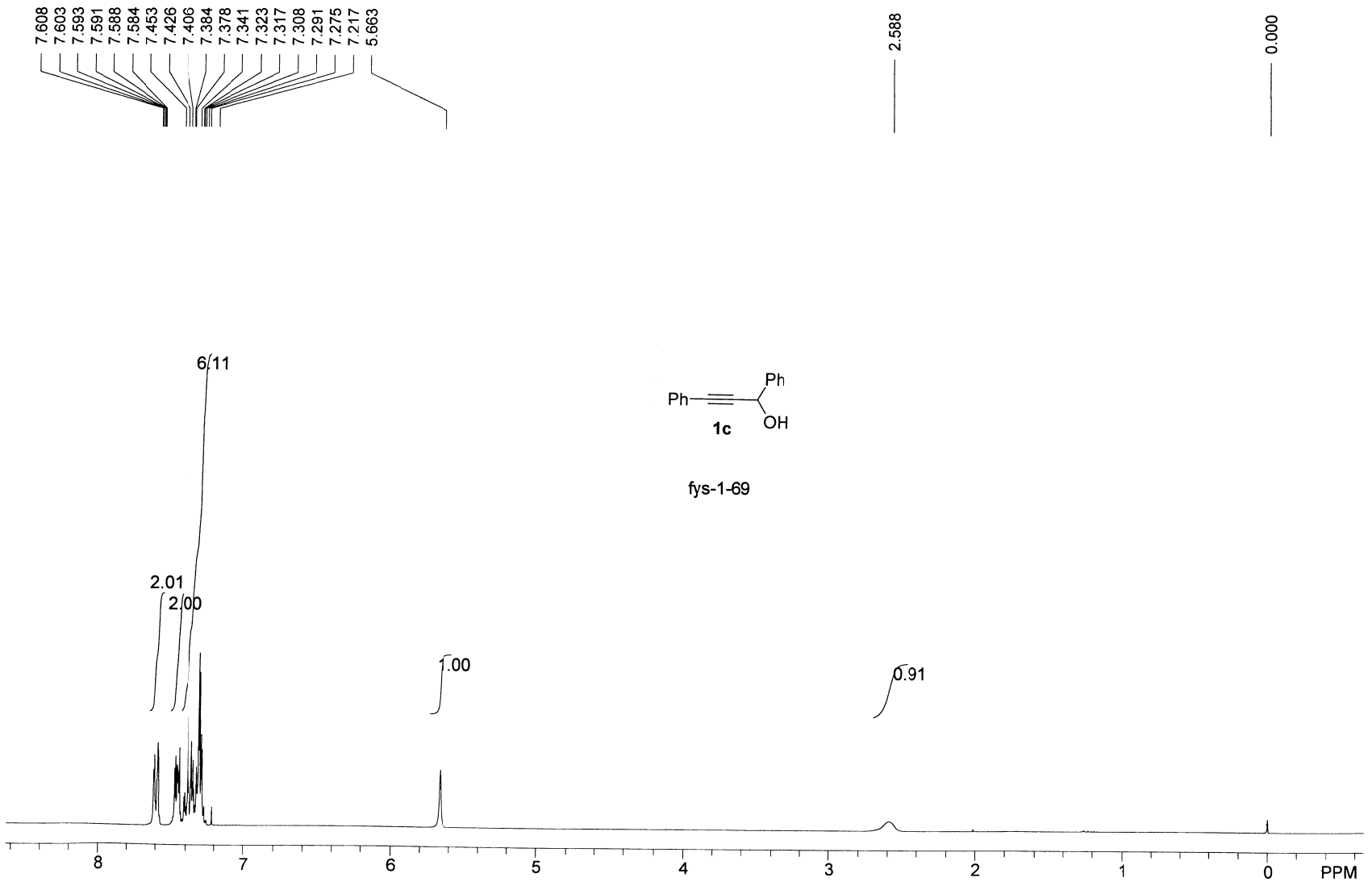
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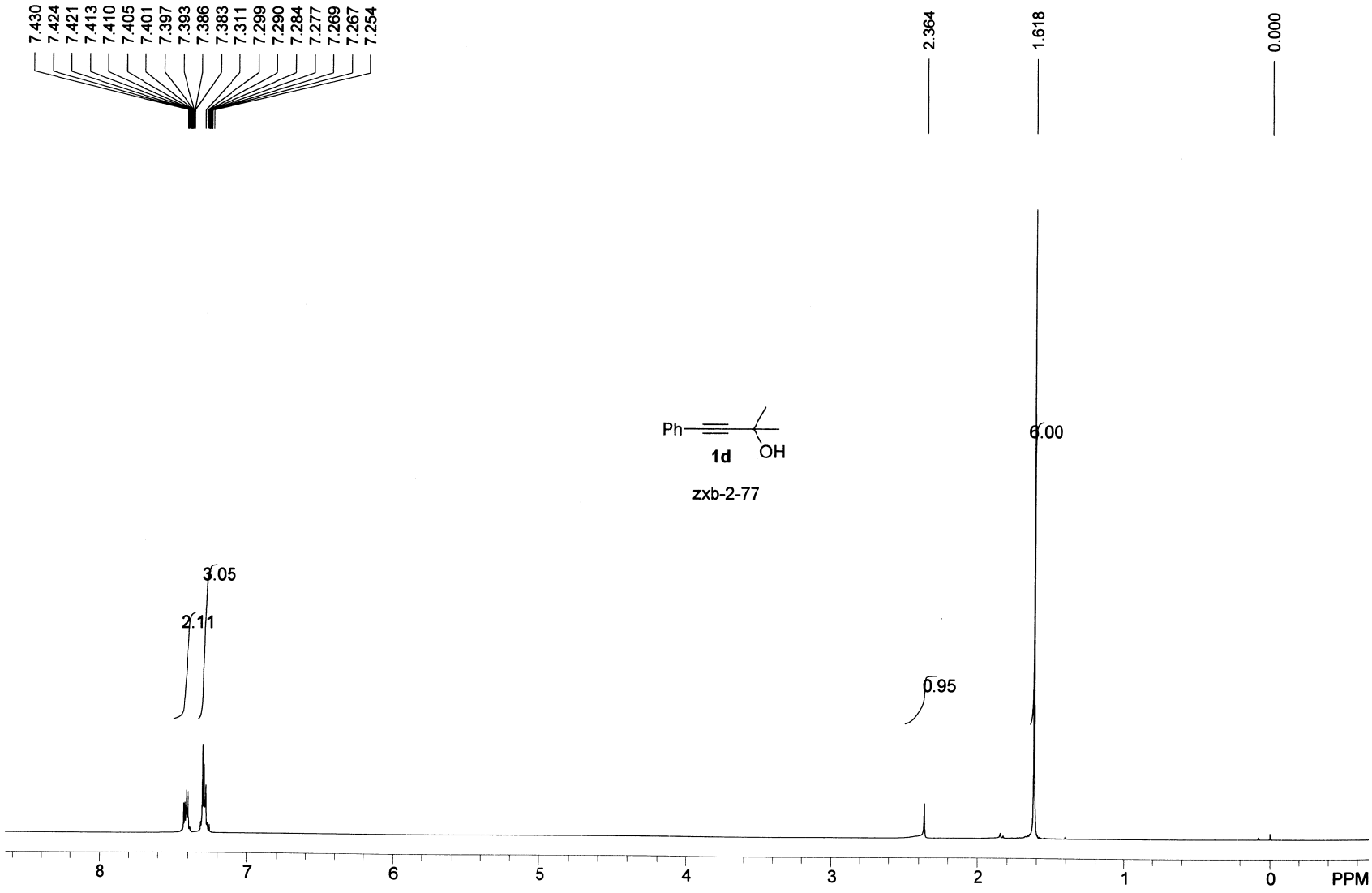
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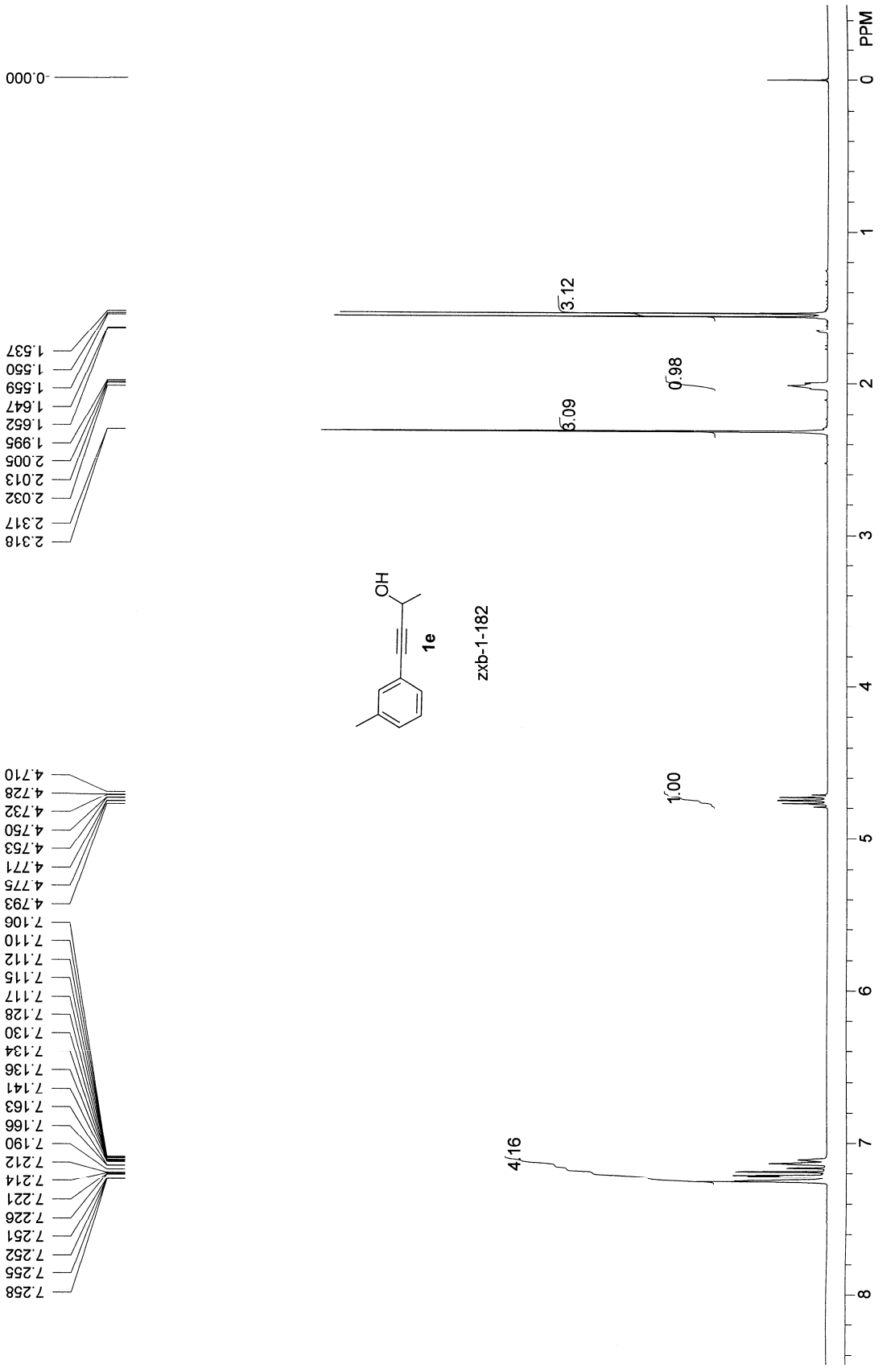
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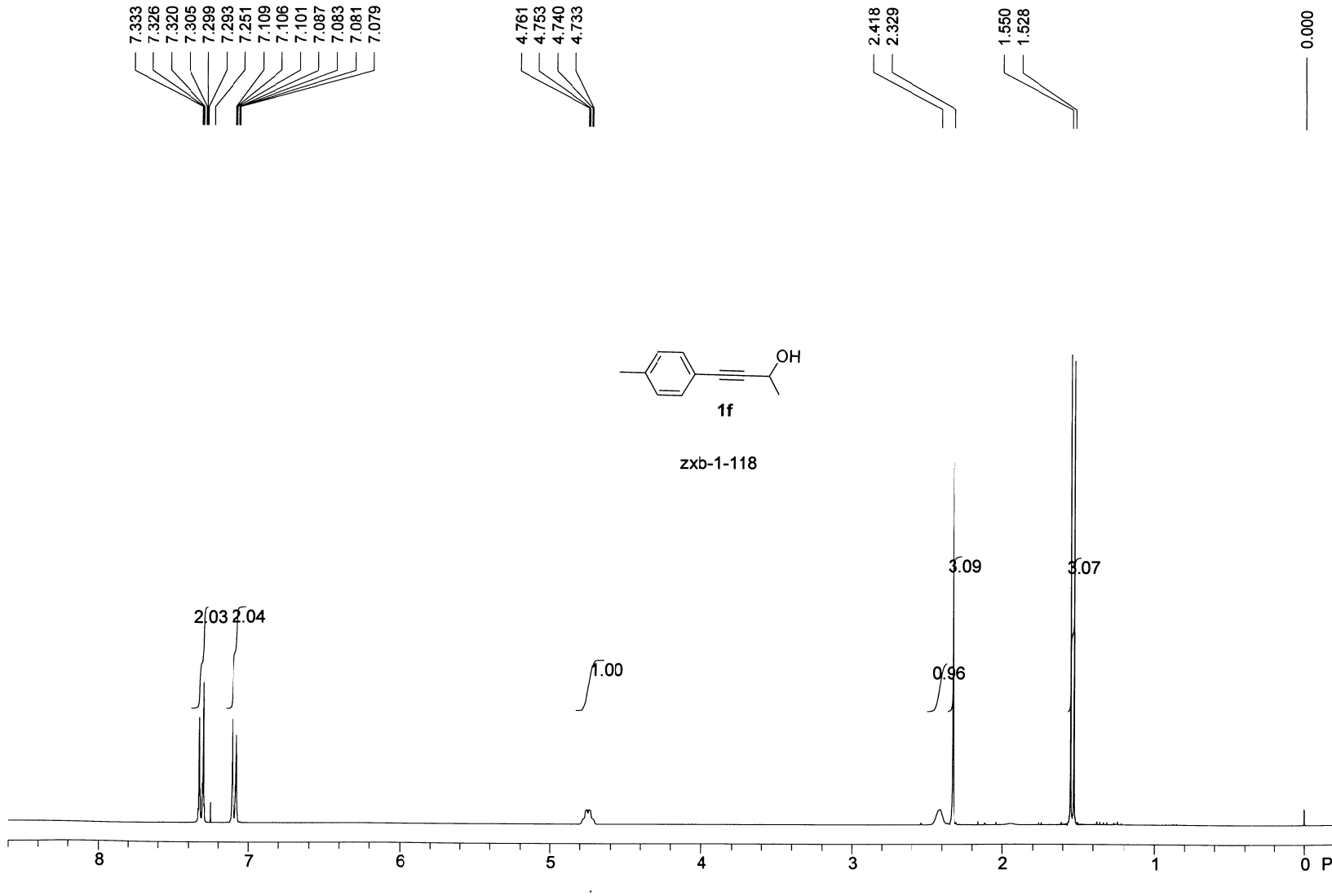
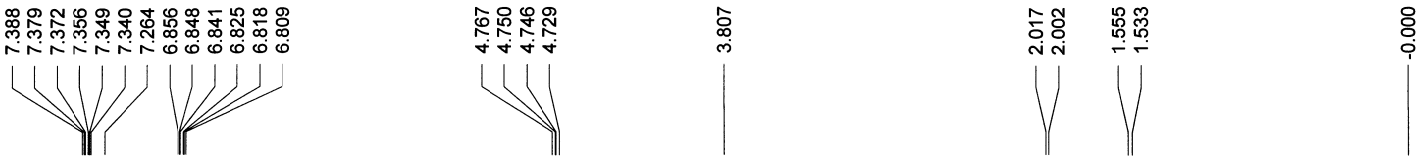
7.255
7.258


7.333
7.326
7.320
7.305
7.299
7.293
7.251
7.109
7.106
7.101
7.087
7.083
7.081
7.079
4.761
4.753
4.740
4.733
2.418
2.329
1.550
1.528
0.000
OH
1f
zxb-1-118
2.03
2.04
1.00
3.09
0.96
3.07
8
7
6
5
4
3
2
1
0 PPM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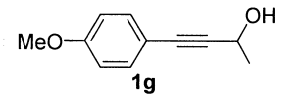
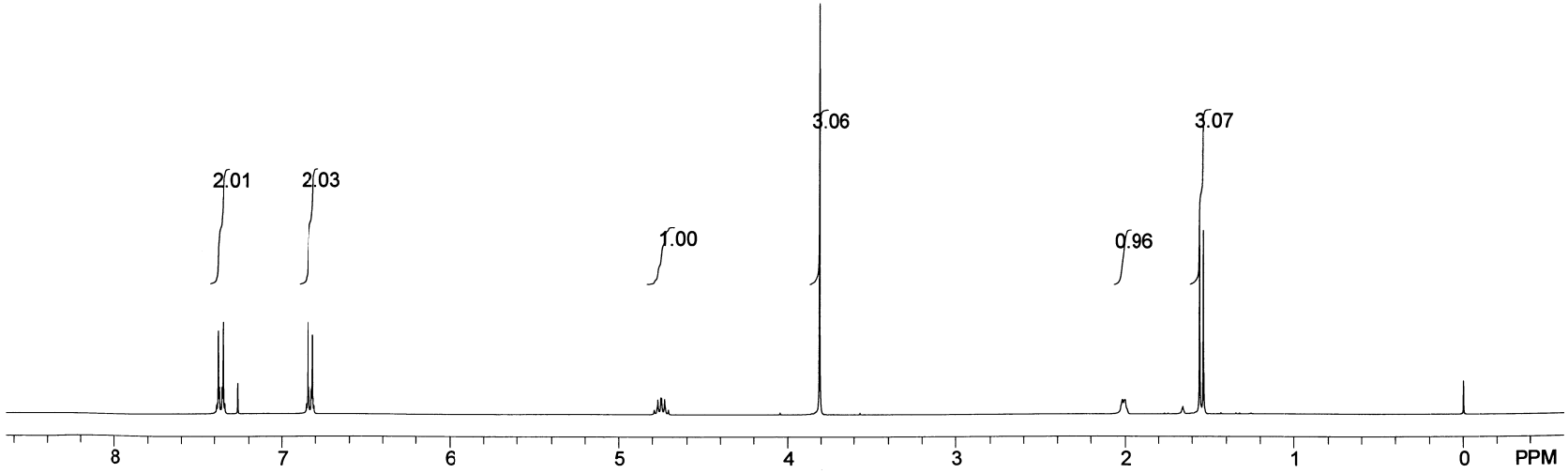
7.379
7.372
7.356
7.349
7.340
7.264
6.856
6.848
6.841
6.825
6.818
6.809
4.767
4.750
4.746
4.729
3.807
2.017
2.002
1.555
1.533
-0.000

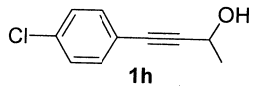

MeO
OH

1g

zxb-1-149

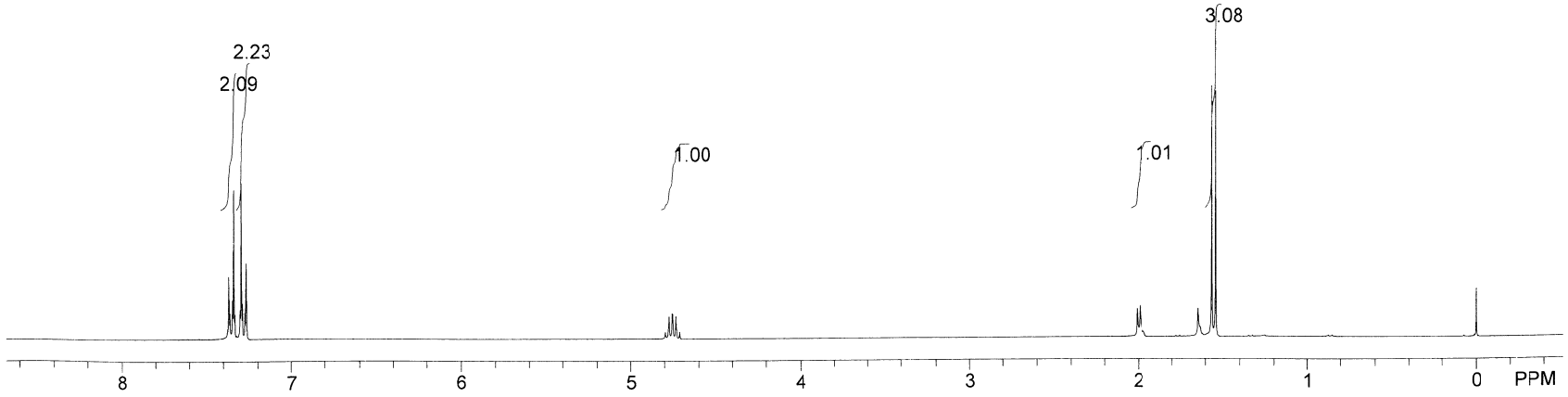

2.01
2.03
1.00
3.06
0.96
3.07
8
7
6
5
4
3
2
1
0
PPM

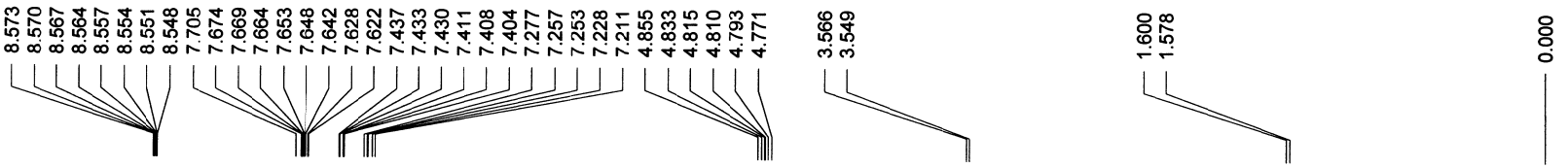

7.369
7.362
7.348
7.340
7.304
7.297
7.290
7.275
7.267
4.755
2.008
1.990
1.564
1.542
0.000

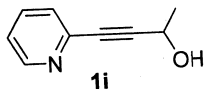

Cl
OH

1h

zxb-1-91

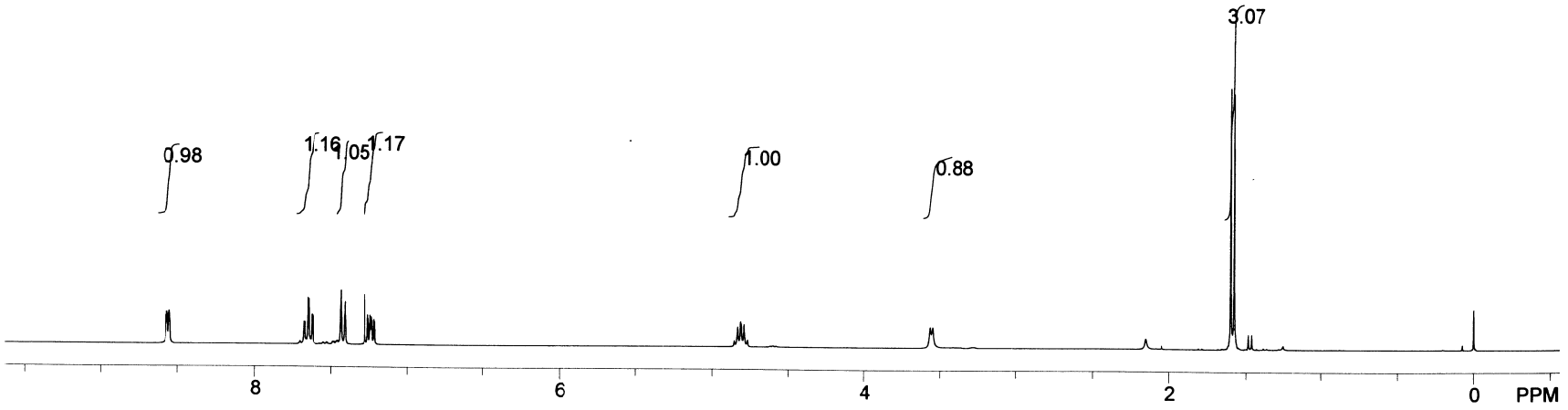

2.23
2.09
1.00
1.01
3.08
8
7
6
5
4
3
2
1
0
PPM


8.573
8.570
8.567
8.564
8.557
8.554
8.551
8.548
7.705
7.674
7.669
7.664
7.653
7.648
7.642
7.628
7.622
7.437
7.433
7.430
7.411
7.408
7.404
7.277
7.257
7.253
7.228
7.211
4.855
4.833
4.815
4.810
4.793
4.771
3.566
3.549
1.600
1.578
0.000

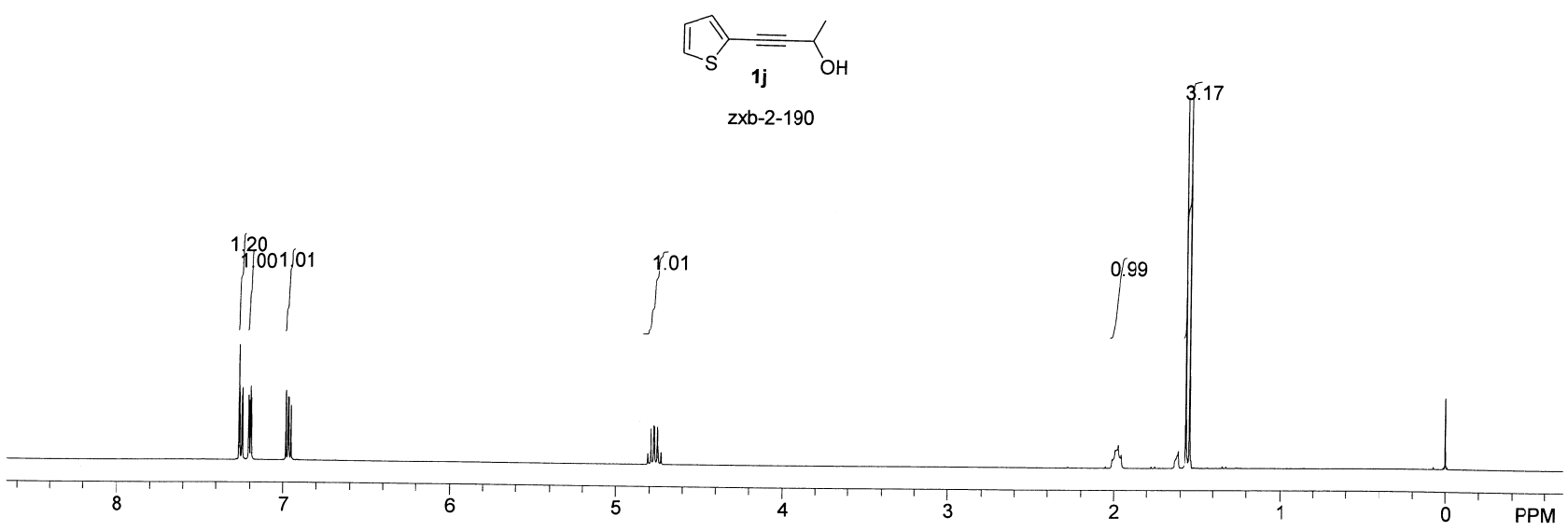

N
OH

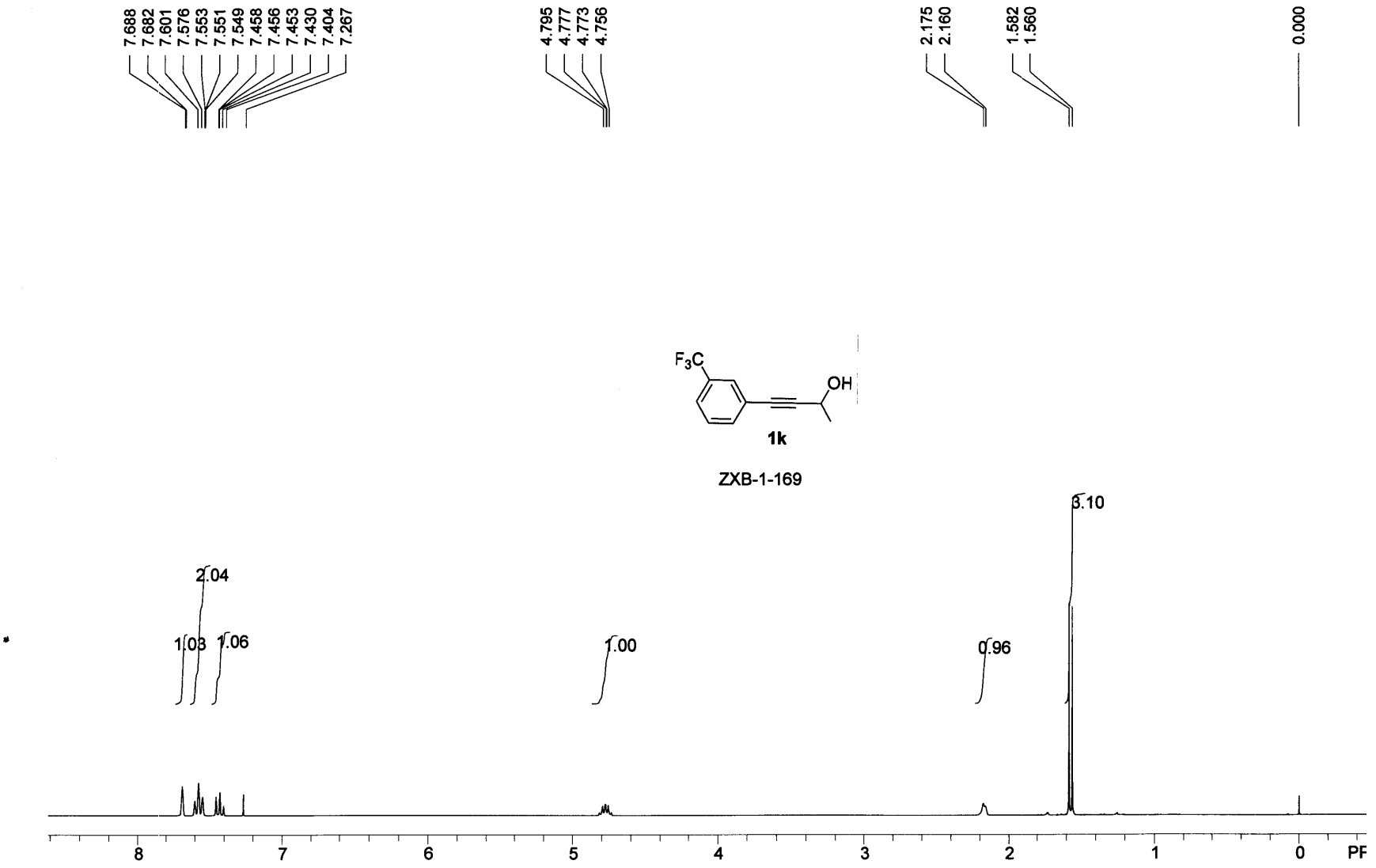
1i

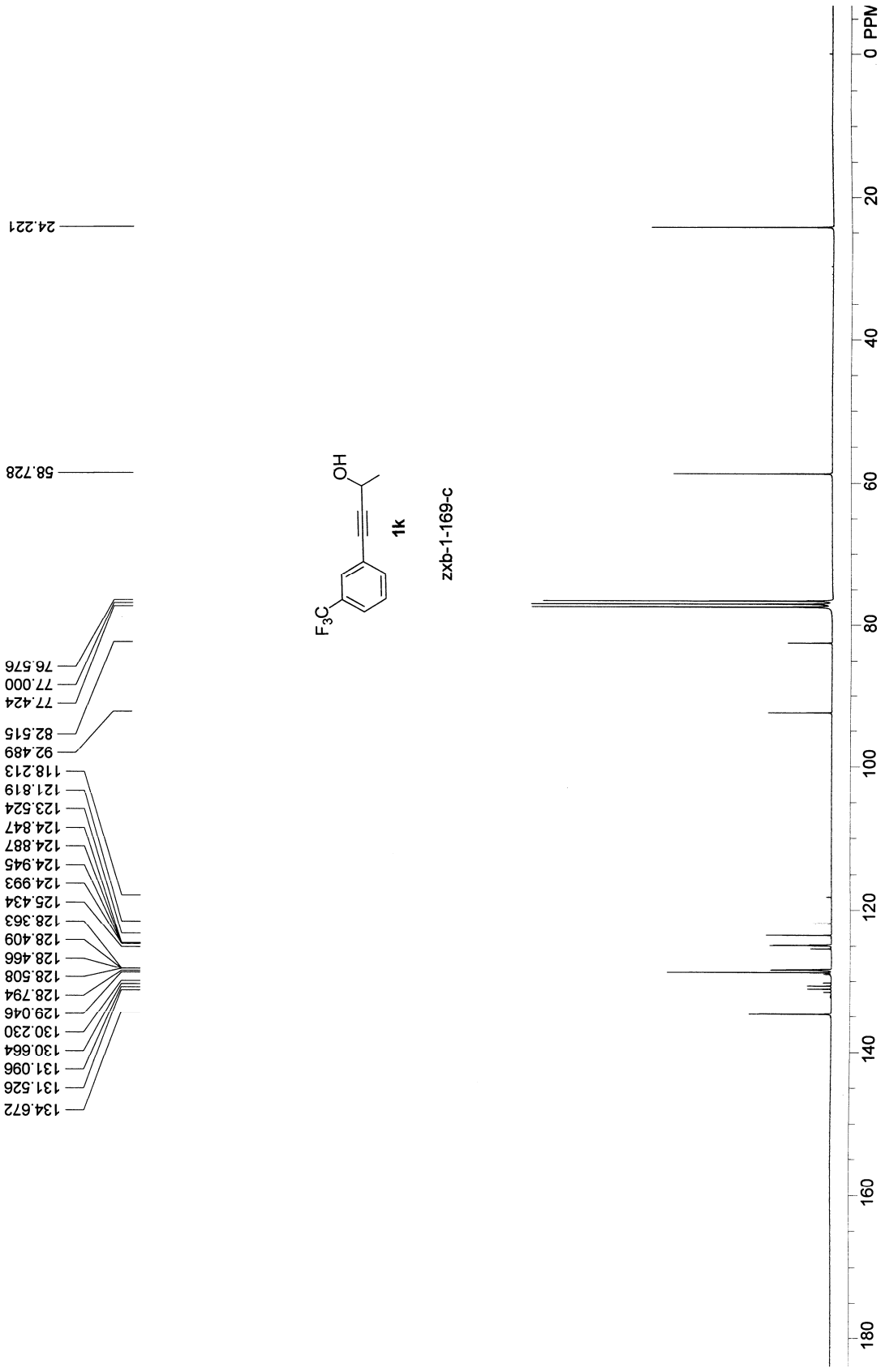
zxb-2-58

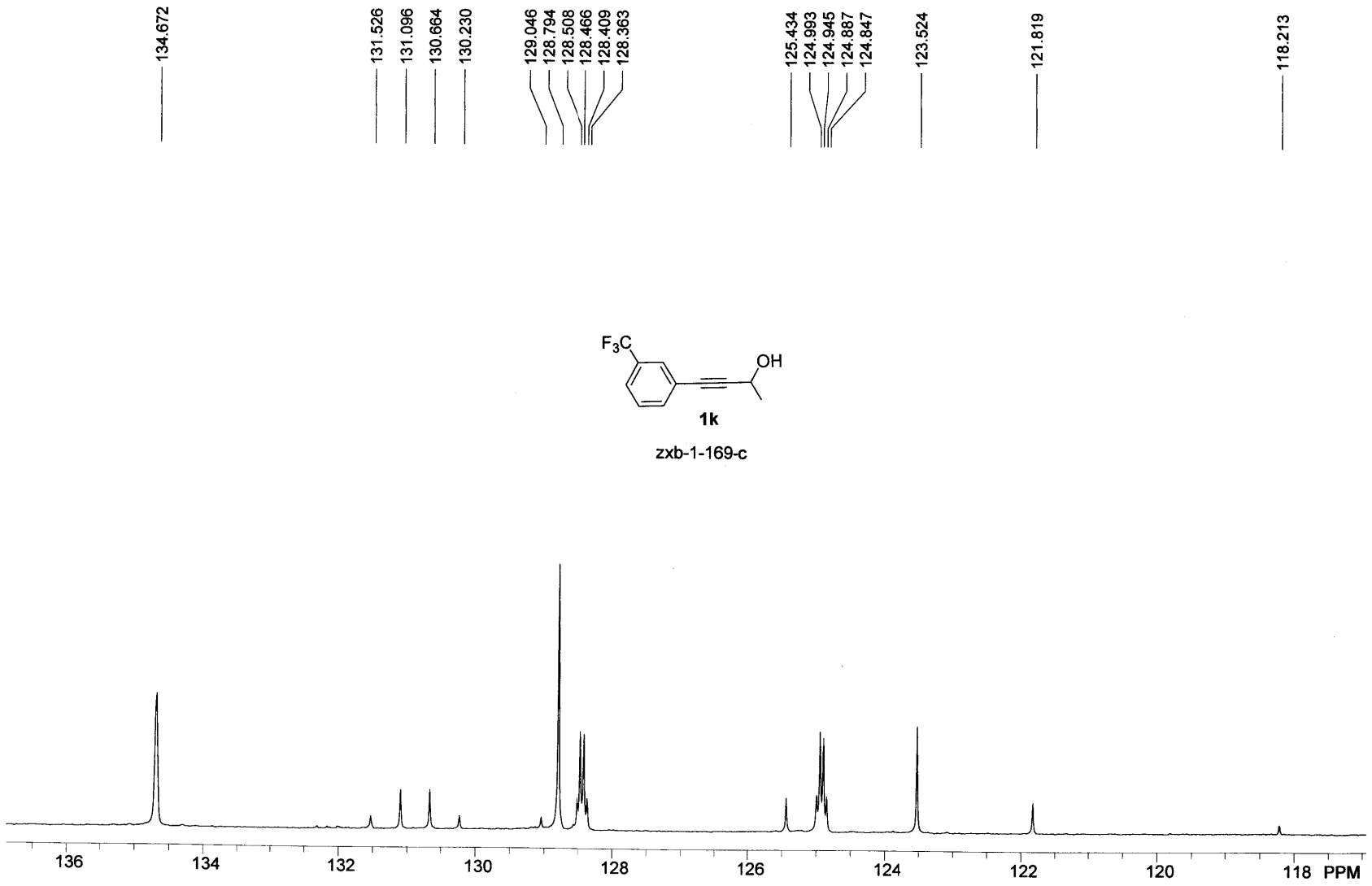

3.07
0.98
1.16
1.05
1.17
1.00
0.88
8
6
4
2
0
PPM


7.263
7.247
7.243
7.208
7.204
7.196
7.192
6.983
6.971
6.966
6.954
4.810
4.792
4.788
4.771
4.766
4.749
4.745
4.726
2.009
1.992
1.983
1.975
1.956
1.562
1.540
-0.000

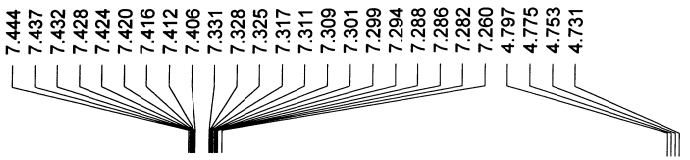

S
OH
1j
zxb-2-190
1.20
1.00
1.01
1.01
0.99
3.17
8
7
6
5
4
3
2
1
0
PPM


7.688
7.682
7.601
7.576
7.553
7.551
7.549
7.458
7.456
7.453
7.430
7.404
7.267
4.795
4.777
4.773
4.756
2.175
2.160
1.582
1.560
0.000
F3C
OH
1k
ZXB-1-169
3.10
2.04
1.03
1.06
1.00
0.96
8
7
6
5
4
3
2
1
0
PF


24.221
58.728
76.576
77.000
77.424
82.515
92.489
118.213
121.819
123.524
124.847
124.887
124.945
124.993
125.434
128.363
128.409
128.466
128.508
128.794
129.046
130.230
130.664
131.096
131.526
134.672
OH
F3C
1k
zxb-1-169-c
0
20
40
60
80
100
120
140
160
180
PPM


134.672
131.526
131.096
130.664
130.230
129.046
128.794
128.508
128.466
128.409
128.363
125.434
124.993
124.945
124.887
124.847
123.524
121.819
118.213
F3C
OH
1k
zxb-1-169-c
136
134
132
130
128
126
124
122
120
118
PPM

-63.020
OH
F3C
1k
zxb-1-169-f
0
-50
-100
-150
-200
PPM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7.437
7.432
7.428
7.424
7.420
7.416
7.412
7.406
7.331
7.328
7.325
7.317
7.311
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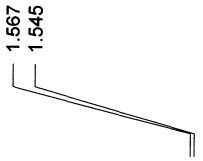
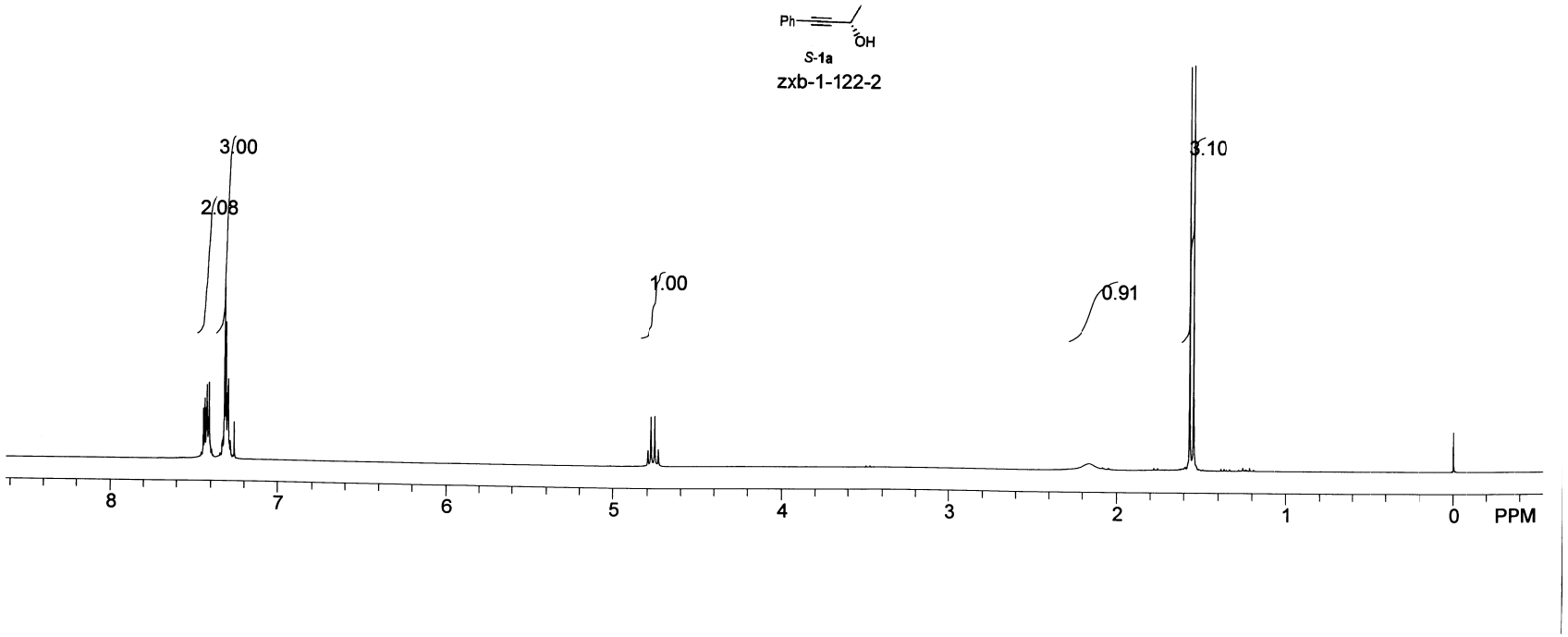
7.260
4.797
4.775
4.753
4.731


1.567
1.545


-0.000


Ph
OH
S-1a
zxb-1-122-2
3.00
2.08
1.00
0.91
3.10
8
7
6
5
4
3
2
1
0
PPM

Data File D:\HPCHEM\1\DATA\ZXB\ZXB00000.D

Sample Name: zxb-1-119-2

n-hexane/i-propanol=90/10; 230 nm; 1.0 ml/min; OJ-H

```
==========================================================================
Injection Date  : 4/10/2008 8:53:29 PM
Sample Name     : zxb-1-119-2                    Location :   -
Acq. Operator   : zxb
Method          : D:\HPCHEM\1\METHODS\ERIC.M
Last changed    : 4/10/2008 8:40:09 PM by cb
                  (modified after loading)
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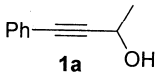
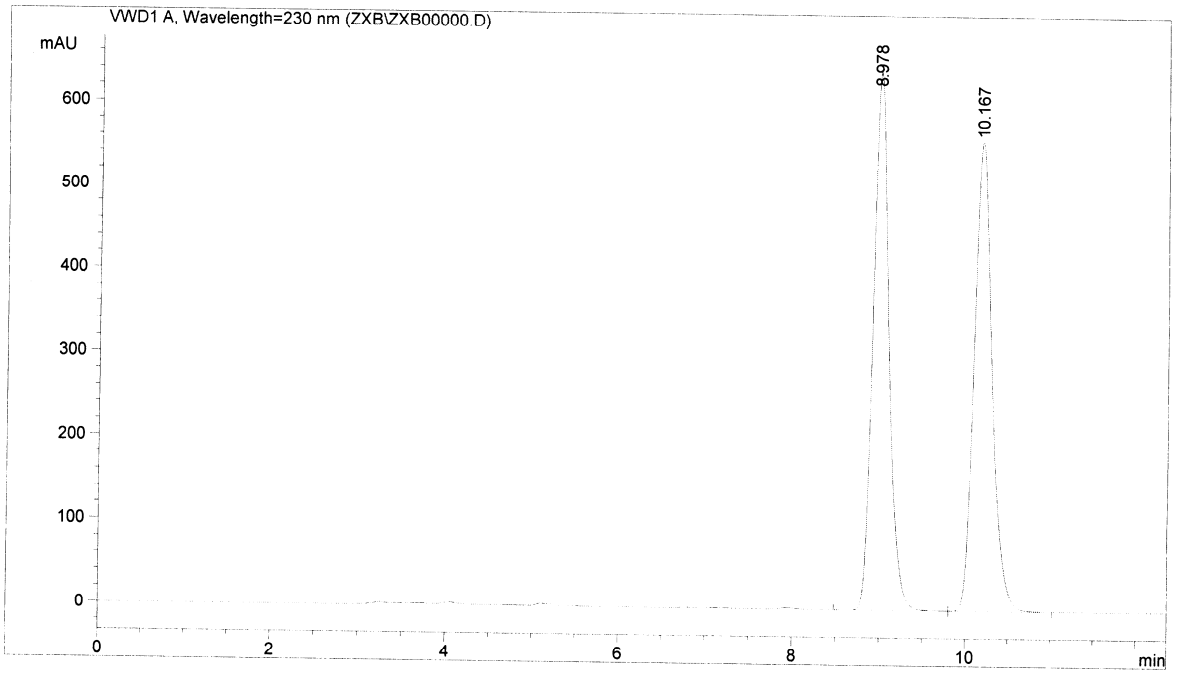


1a




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

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


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   8.978 BV    0.1916 8165.71045  643.88654  49.9350
   2  10.167 VB    0.2213 8186.96094  560.62018  50.0650

Totals :                  1.63527e4  1204.50671

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

Instrument 1 4/10/2008 9:12:49 PM zxb

Page 1 of 1

Data File D:\HPCHEM\1\DATA\ZXB\ZXB00001.D

Sample Name: zxb-1-122-2

n-hexane/i-propanol=90/10; 230 nm; 1.0 ml/min; OJ-H

```
==========================================================================
Injection Date  : 4/10/2008 9:08:34 PM
Sample Name     : zxb-1-122-2                    Location :   -
Acq. Operator   : zxb
Method          : D:\HPCHEM\1\METHODS\ERIC.M
Last changed    : 4/10/2008 8:40:09 PM by cb
                  (modified after loading)
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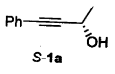
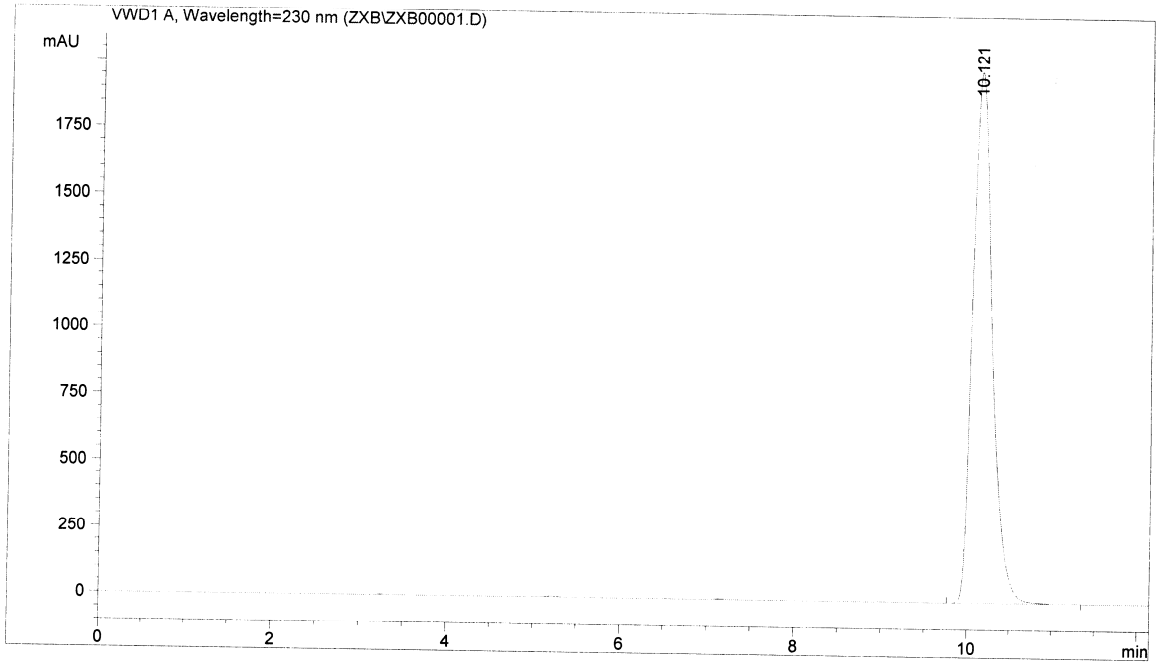


S-1a




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

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

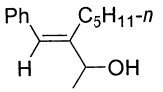

Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  10.121 BB    0.2467 3.20112e4  1997.00330 100.0000

Totals :                  3.20112e4  1997.00330

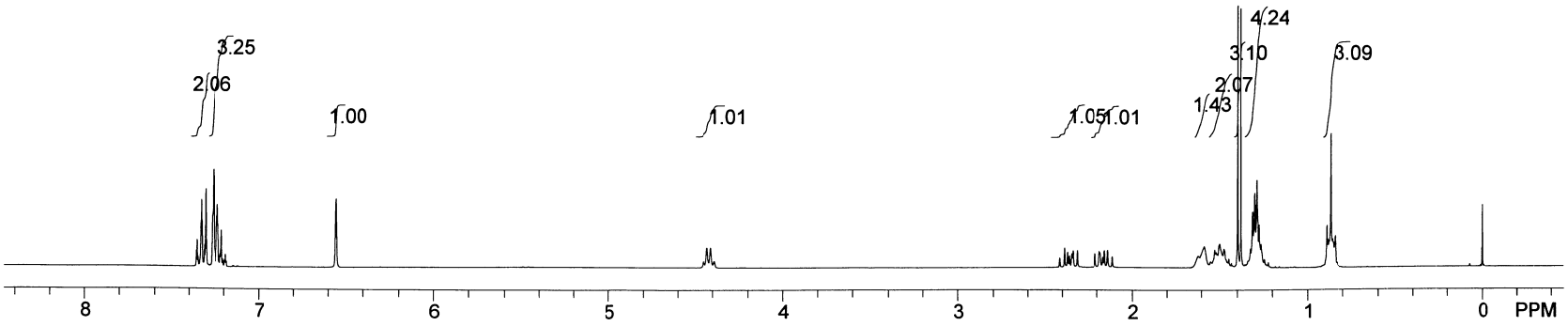
 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

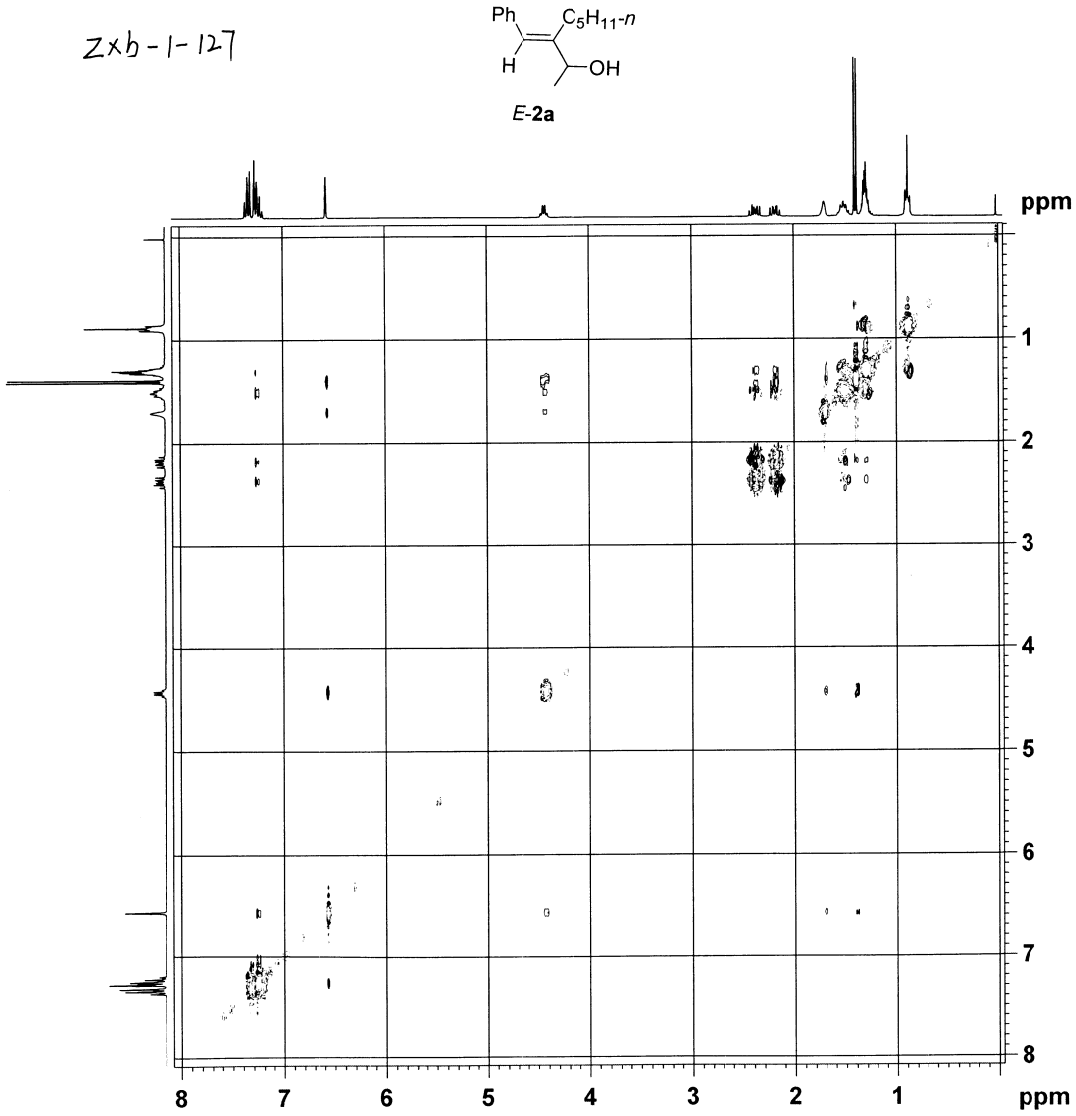

7.356
7.332
7.308
7.263
7.259
7.239
7.214
7.191
6.557
4.455
4.433
4.413
4.391
2.414
2.387
2.338
2.314
2.211
2.181
2.157
2.111
1.605
1.549
1.525
1.511
1.500
1.474
1.396
1.374
1.308
1.297
1.284
1.261
0.892
0.868
0.845
0.000

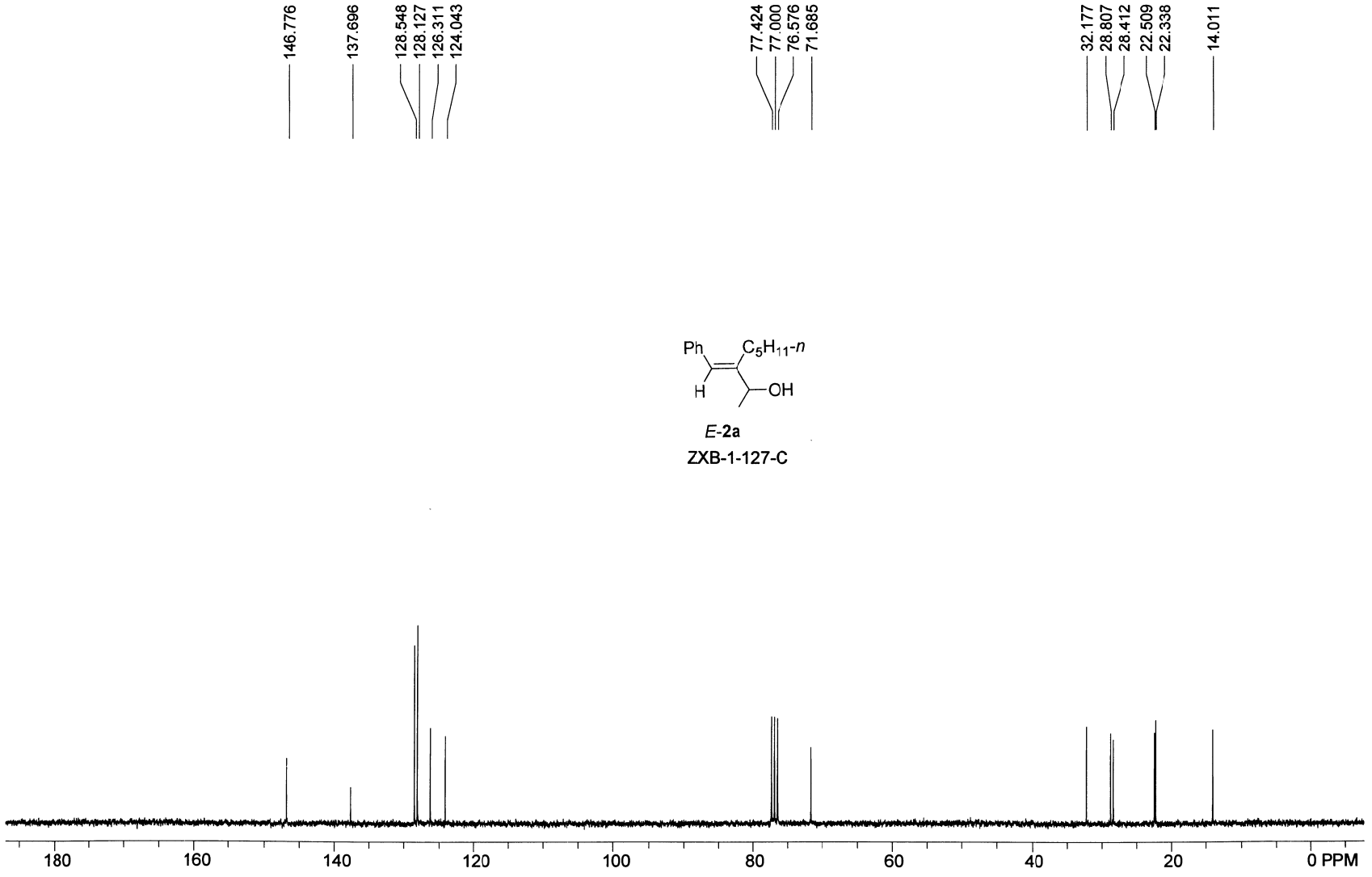

Ph
C5H11-n
H
OH

E-**2a**

zxb-1-127


2.06
3.25
1.00
1.01
1.05
1.01
1.43
2.07
3.10
4.24
3.09
8
7
6
5
4
3
2
1
0
PPM


Zxb-1-127
Ph
C_5H_{11}-*n*
H
OH
E-**2a**
ppm
1
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
ppm


146.776
137.696
128.548
128.127
126.311
124.043
77.424
77.000
76.576
71.685
32.177
28.807
28.412
22.509
22.338
14.011
Ph
C5H11-n
H
OH
E-2a
ZXB-1-127-C
180
160
140
120
100
80
60
40
20
0 PPM


7.252
7.252
7.249
7.247
7.244
7.234
7.232
7.230
7.228
7.014
7.002
6.985
6.972
6.969
6.959
6.957
6.672
4.414
4.393
4.372
4.351
2.525
2.494
2.470
2.424
2.333
2.298
2.279
2.233
1.704
1.569
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1.457
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1.377
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0.914
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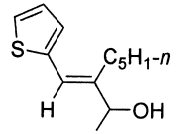
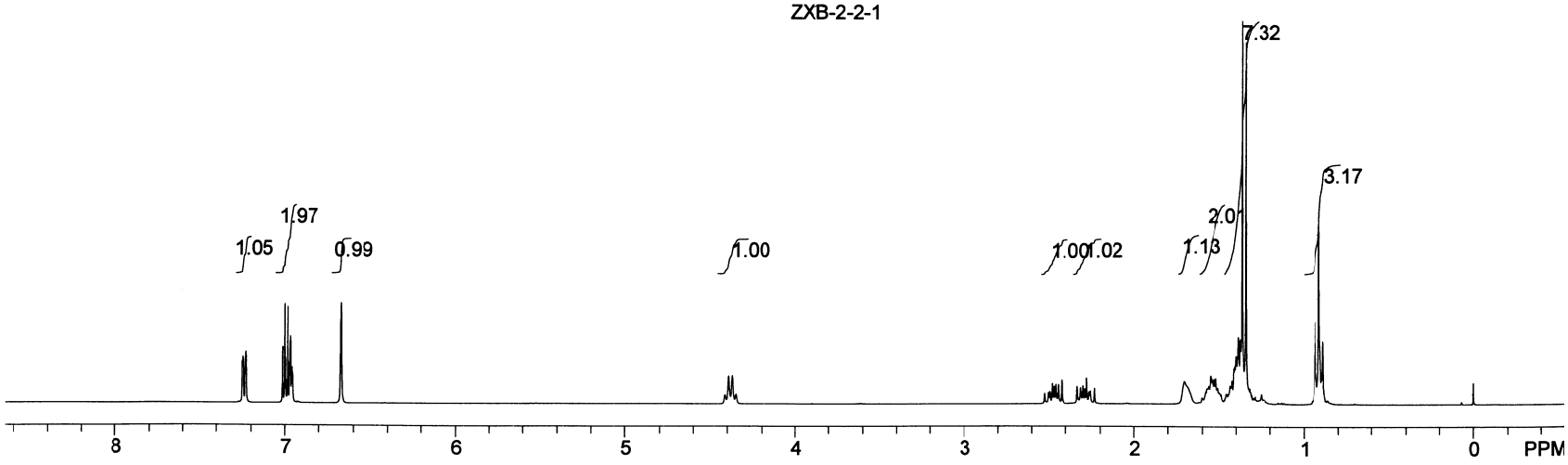
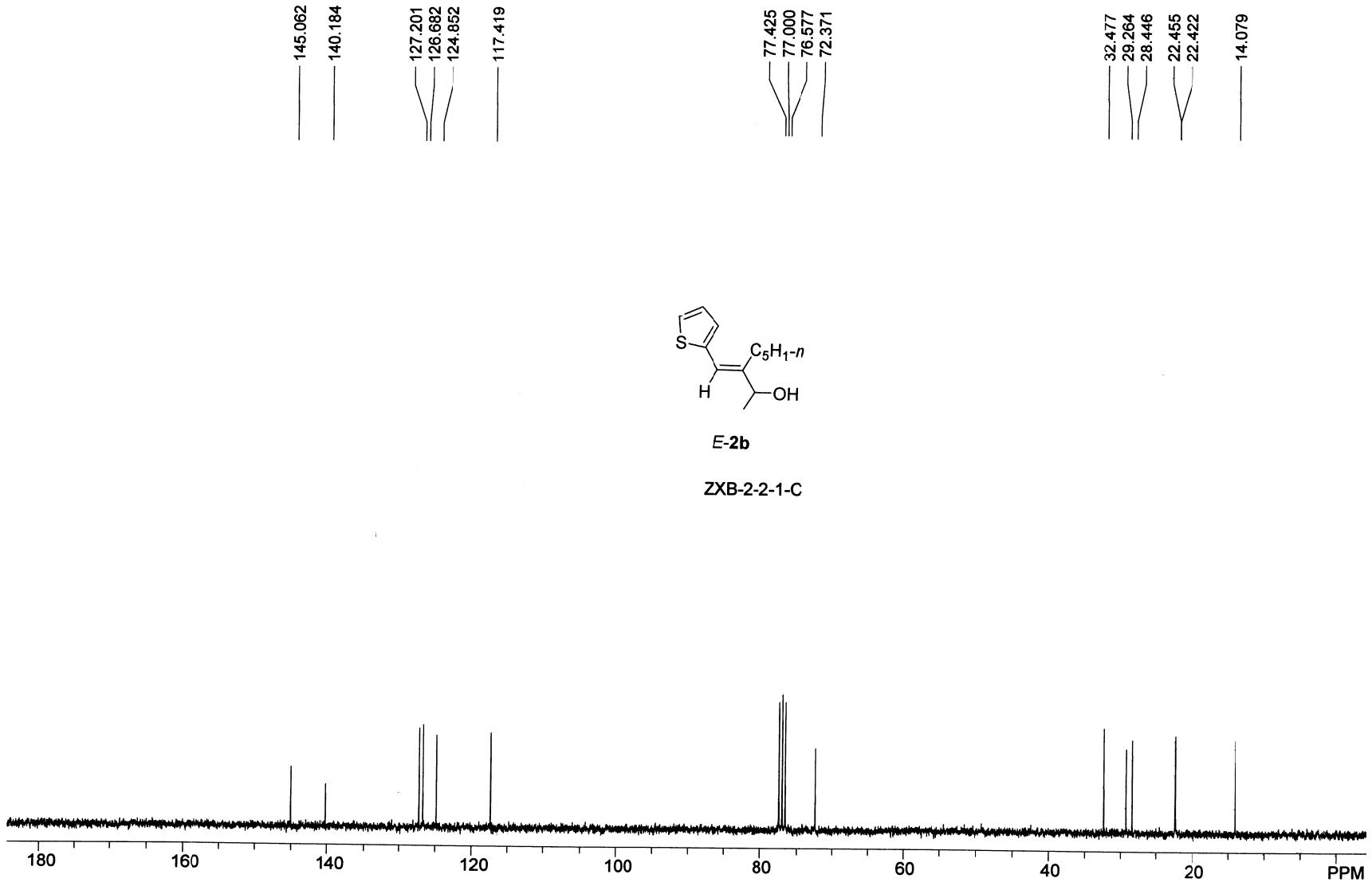
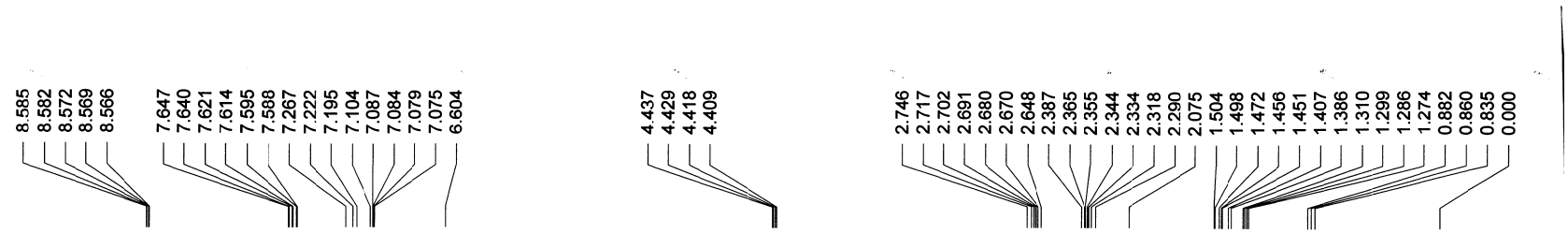
0.000


S
C_5H_1-*n*
H
OH

E-**2b**


ZXB-2-2-1
7.32
3.17
2.0
1.97
1.05
0.99
1.00
1.00
1.02
1.13
8
7
6
5
4
3
2
1
0
PPM


145.062
140.184
127.201
126.682
124.852
117.419
77.425
77.000
76.577
72.371
32.477
29.264
28.446
22.455
22.422
14.079
S
C_5H_{1-n}
H
OH
E-**2b**
ZXB-2-2-1-C
180
160
140
120
100
80
60
40
20
PPM


8.585
8.582
8.572
8.569
8.566
7.647
7.640
7.621
7.614
7.595
7.588
7.267
7.222
7.195
7.104
7.087
7.084
7.079
7.075
6.604
4.437
4.429
4.418
4.409
2.746
2.717
2.702
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2.670
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2.387
2.365
2.355
2.344
2.334
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1.504
1.498
1.472
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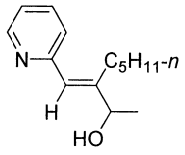
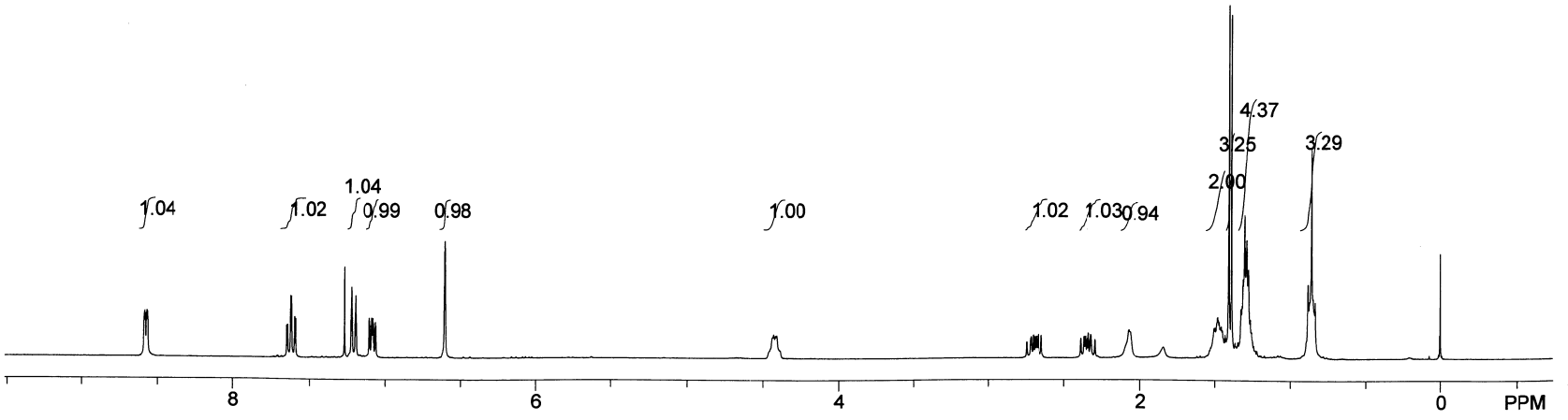
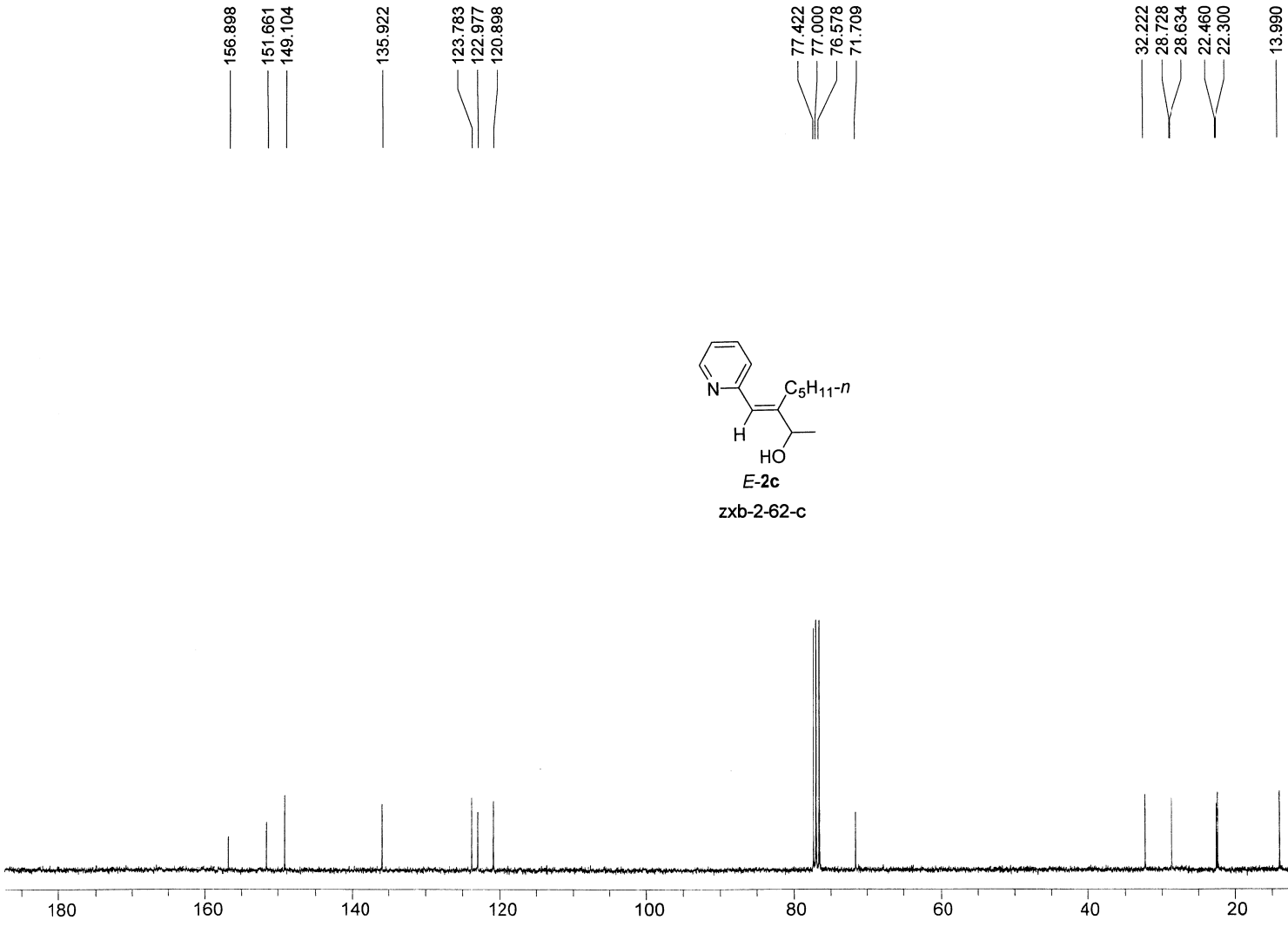
0.835
0.000

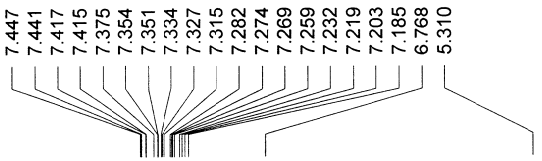

N
C_5H_{11}-*n*
H
HO

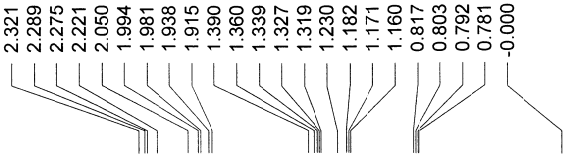
E-**2c**

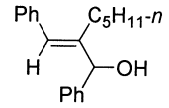
zxb-2-62


1.04
1.02
1.04
0.99
0.98
1.00
1.02
1.03
0.94
2.00
3.25
4.37
3.29
8
6
4
2
0
PPM


156.898
151.661
149.104
135.922
123.783
122.977
120.898
77.422
77.000
76.578
71.709
32.222
28.728
28.634
22.460
22.300
13.990
N
C_5H_{11}-*n*
H
HO
E-**2c**
zxb-2-62-c
180
160
140
120
100
80
60
40
20
0PPM

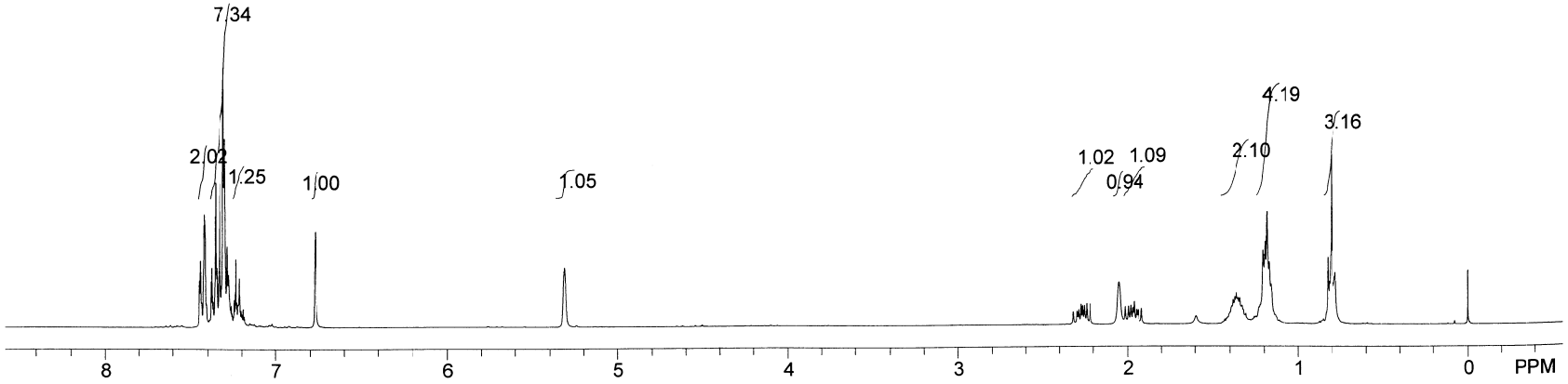

7.447
7.441
7.417
7.415
7.375
7.354
7.351
7.334
7.327
7.315
7.282
7.274
7.269
7.259
7.232
7.219
7.203
7.185
6.768
5.310

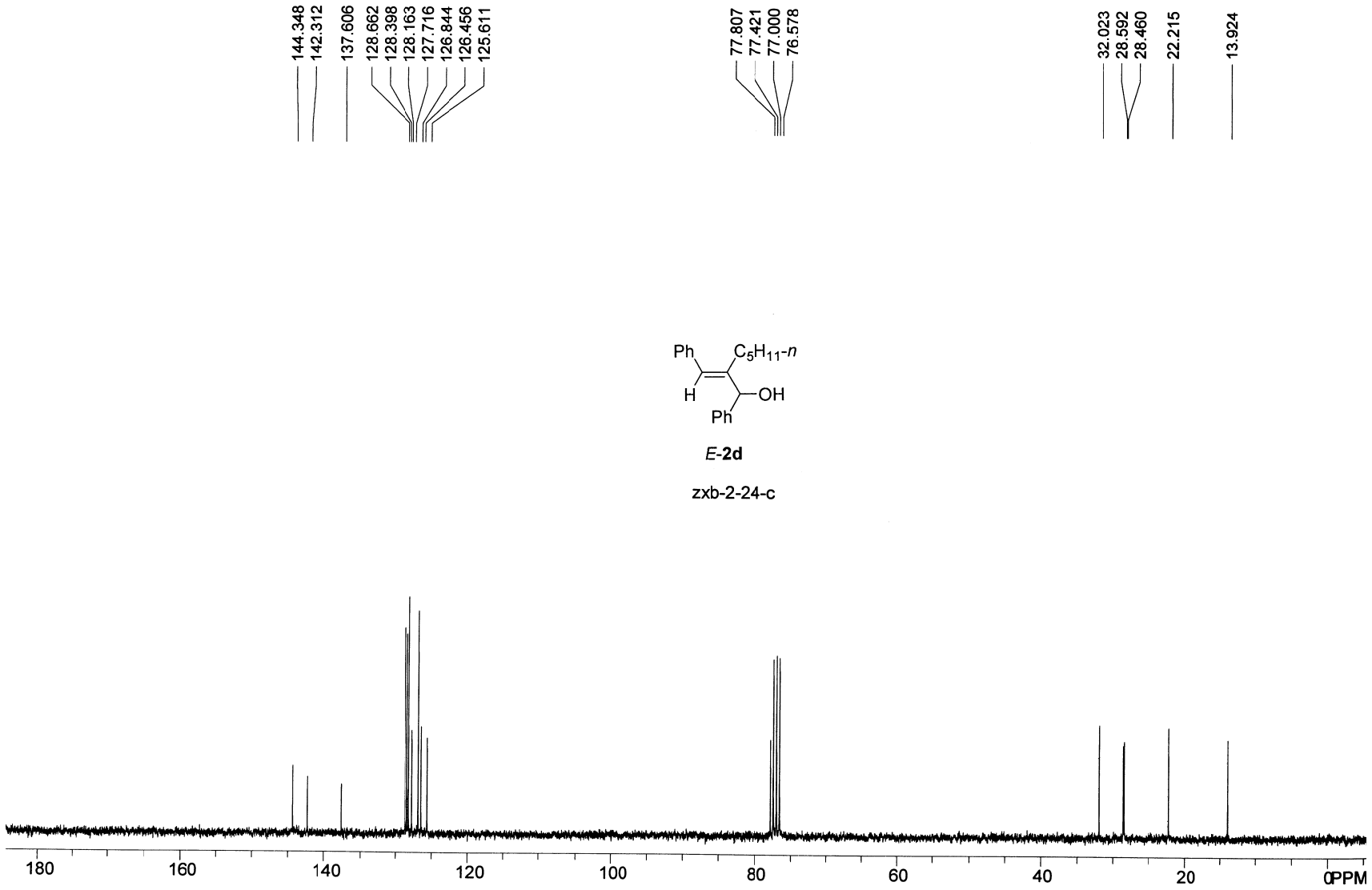

2.321
2.289
2.275
2.221
2.050
1.994
1.981
1.938
1.915
1.390
1.360
1.339
1.327
1.319
1.230
1.182
1.171
1.160
0.817
0.803
0.792
0.781
-0.000

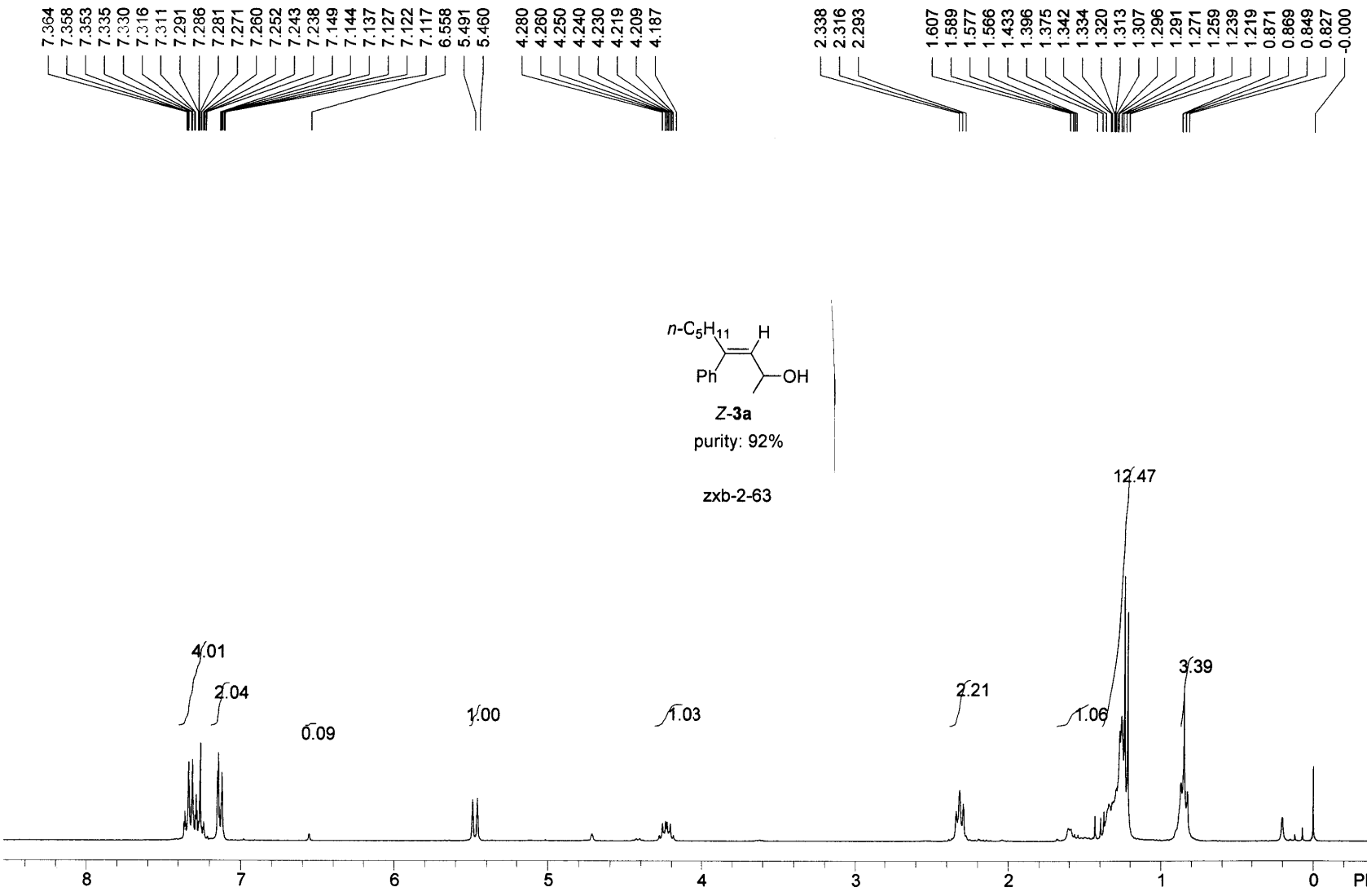

Ph
C5H11-n
H
OH
Ph

E-**2d**

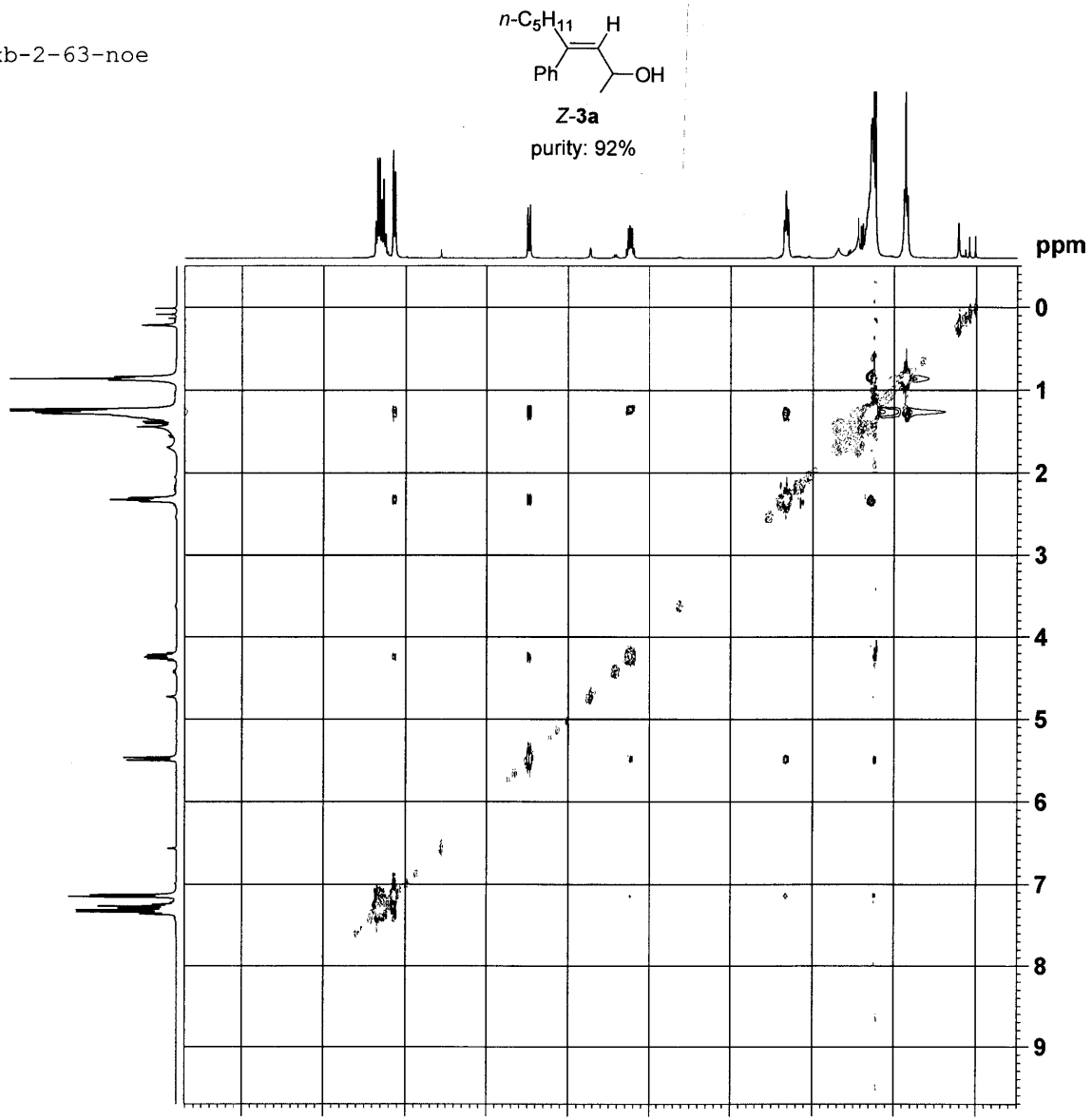
zxb-2-24-1

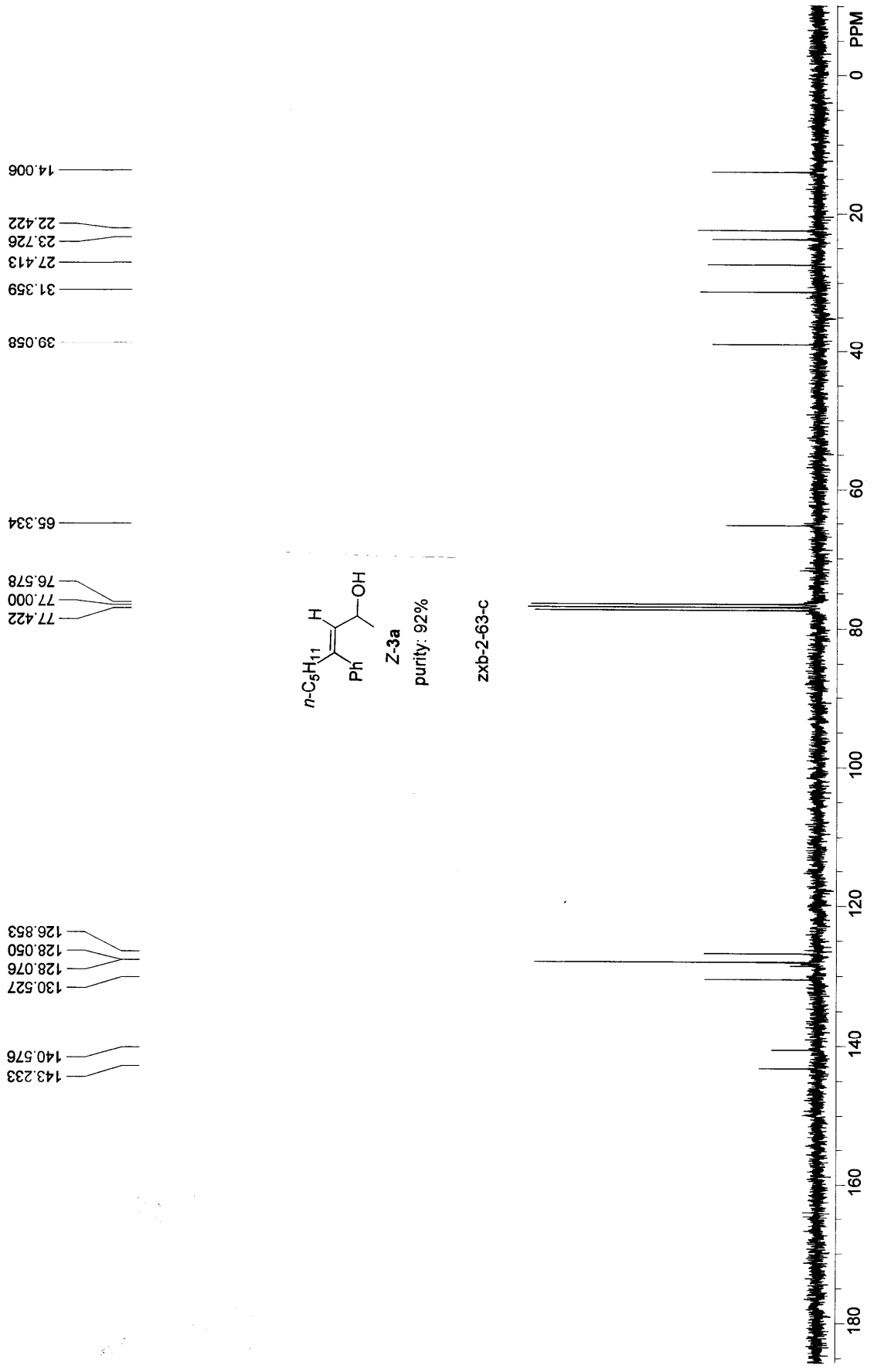

7.34
2.02
1.25
1.00
1.05
1.02
1.09
0.94
2.10
4.19
3.16
8
7
6
5
4
3
2
1
0
PPM


144.348
142.312
137.606
128.662
128.398
128.163
127.716
126.844
126.456
125.611
77.807
77.421
77.000
76.578
32.023
28.592
28.460
22.215
13.924
Ph
C5H11-n
H
OH
Ph
E-2d
zxb-2-24-c
180
160
140
120
100
80
60
40
20
0PPM

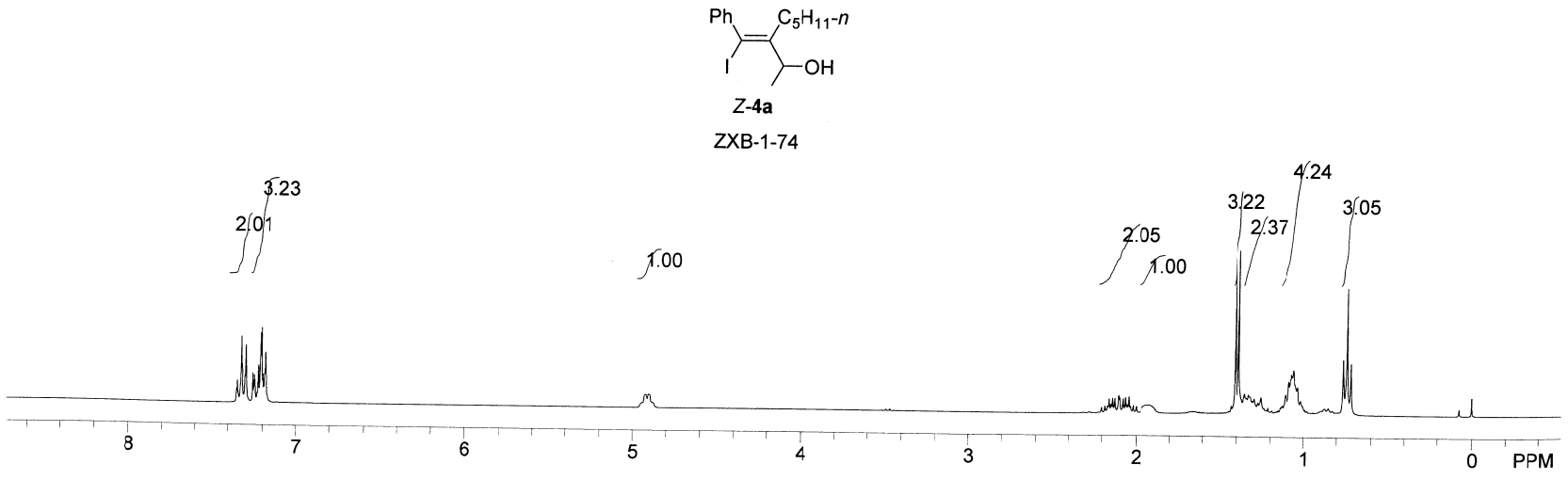

7.364
7.358
7.353
7.335
7.330
7.316
7.311
7.291
7.286
7.281
7.271
7.260
7.252
7.243
7.238
7.149
7.144
7.137
7.127
7.122
7.117
6.558
5.491
5.460
4.280
4.260
4.250
4.240
4.230
4.219
4.209
4.187
2.338
2.316
2.293
1.607
1.589
1.577
1.566
1.433
1.396
1.375
1.342
1.334
1.320
1.313
1.307
1.296
1.291
1.271
1.259
1.239
1.219
0.871
0.869
0.849
0.827
-0.000
n-C5H11
H
Ph
OH
Z-3a
purity: 92%
zxb-2-63
4.01
2.04
0.09
1.00
1.03
2.21
1.06
12.47
3.39
8
7
6
5
4
3
2
1
0
PPM

zxb-2-63-noe

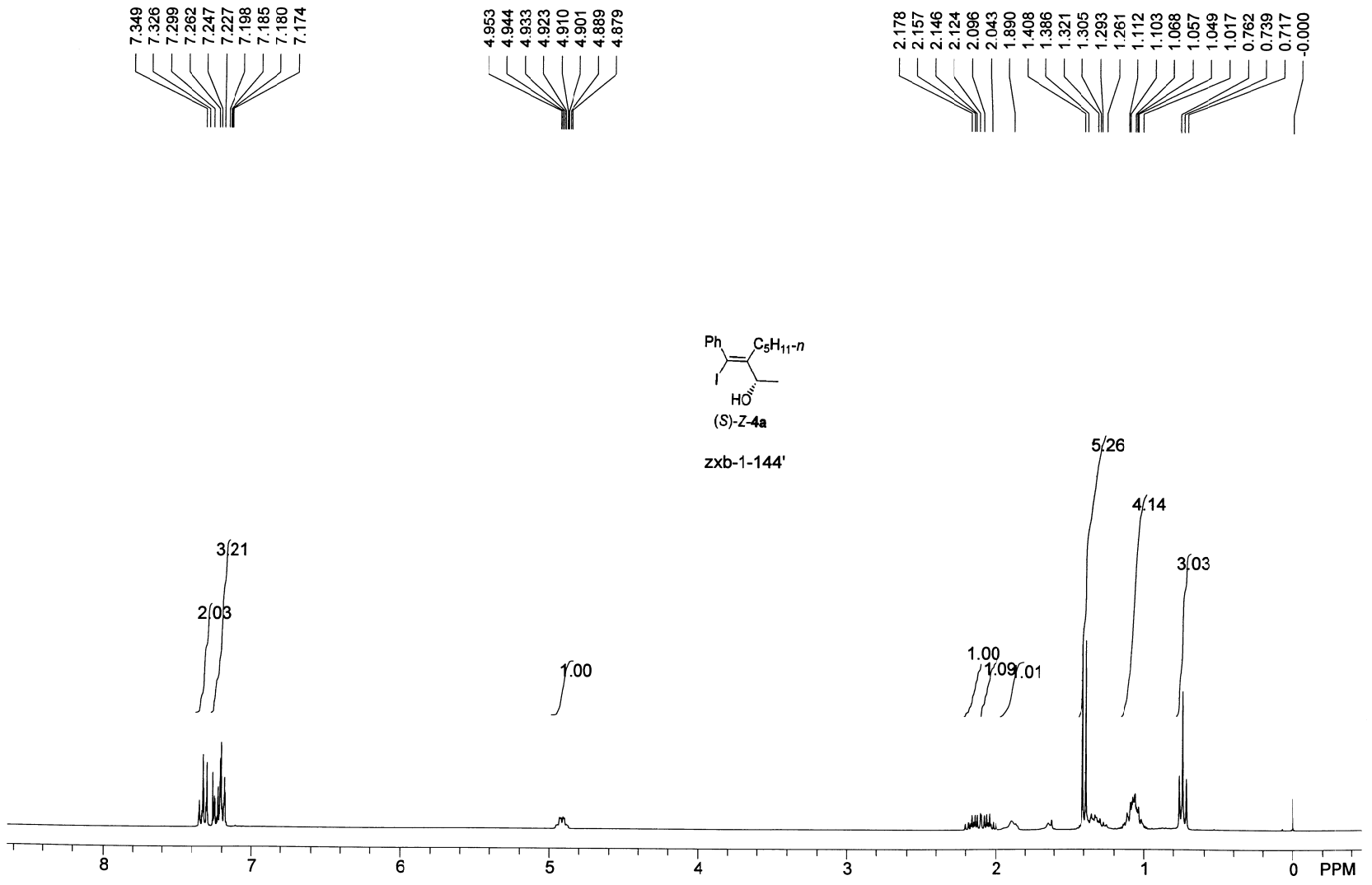


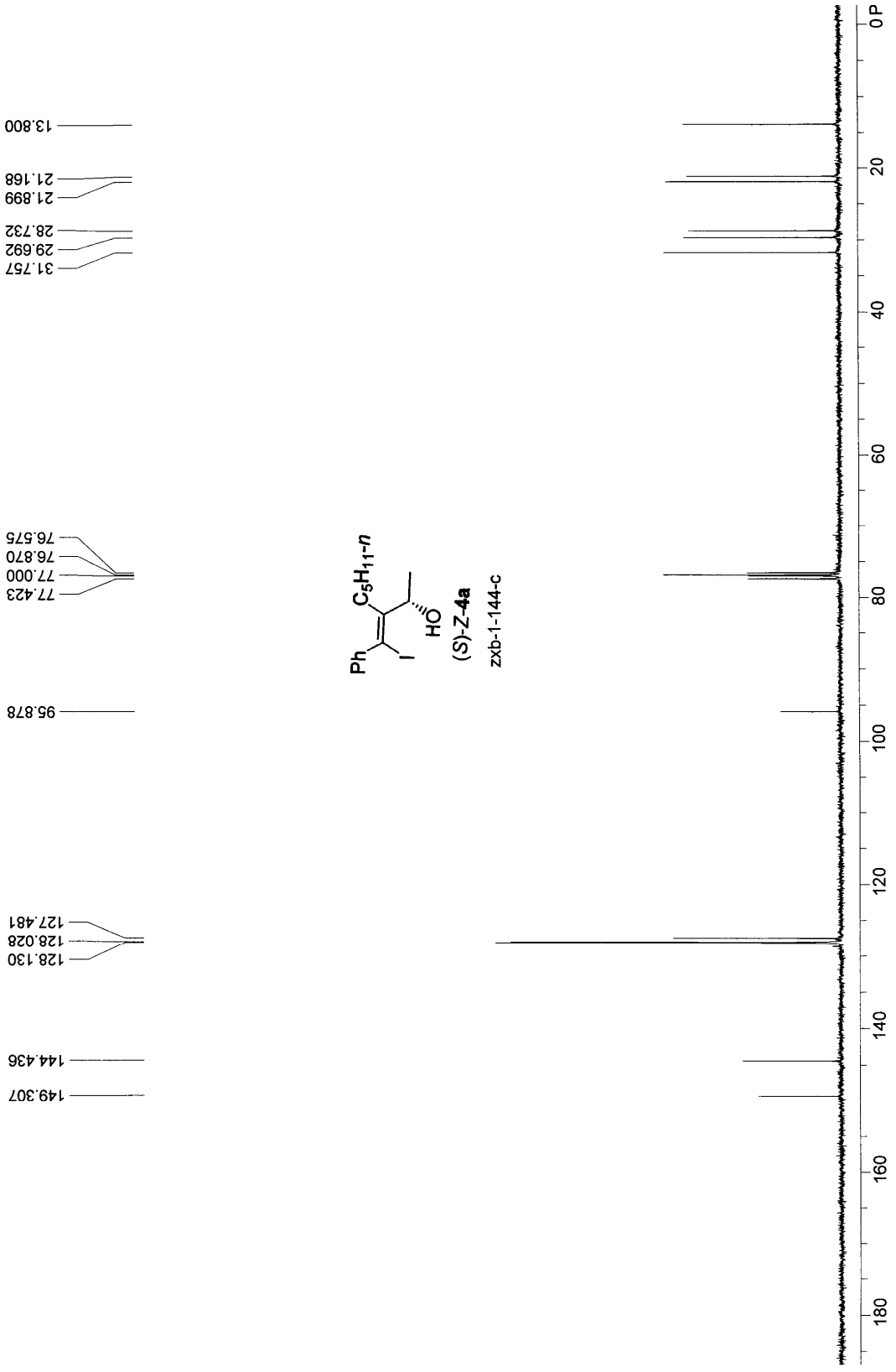

14.006
22.422
23.726
27.413
31.359
39.058
65.334
76.578
77.000
77.422
126.853
128.050
128.076
130.527
140.576
143.233
PPM
0
20
40
60
80
100
120
140
160
180
OH
H
n-C5H11
Ph
Z-3a
purity: 92%
zxb-2-63-c


7.342
7.329
7.254
7.200
7.190
7.184
4.931
4.924
4.910
4.903
2.138
2.103
2.098
2.077
1.928
1.407
1.386
1.349
1.306
1.294
1.271
1.253
1.130
1.111
1.073
1.068
1.060
1.045
1.017
0.762
0.739
0.716
-0.000


Ph
C5H11-n
I
OH
Z-4a
ZXB-1-74
3.23
2.01
1.00
2.05
1.00
3.22
2.37
4.24
3.05
8
7
6
5
4
3
2
1
0
PPM

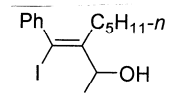
13.827
21.211
21.963
28.811
29.763
31.826
76.577
77.000
77.421
96.040
127.567
128.087
128.208
144.516
149.323
Ph
C_5H_{11}-*n*
OH
I
Z-4a
zxb-1-74
0PPM
20
40
60
80
100
120
140
160
180


7.349
7.326
7.299
7.262
7.247
7.227
7.198
7.185
7.180
7.174
4.953
4.944
4.933
4.923
4.910
4.901
4.889
4.879
2.178
2.157
2.146
2.124
2.096
2.043
1.890
1.408
1.386
1.321
1.305
1.293
1.261
1.112
1.103
1.068
1.057
1.049
1.017
0.762
0.739
0.717
-0.000
Ph
C5H11-n
I
HO
(S)-Z-4a
zxb-1-144'
3.21
2.03
1.00
1.00
1.09
1.01
5.26
4.14
3.03
8
7
6
5
4
3
2
1
0
PPM

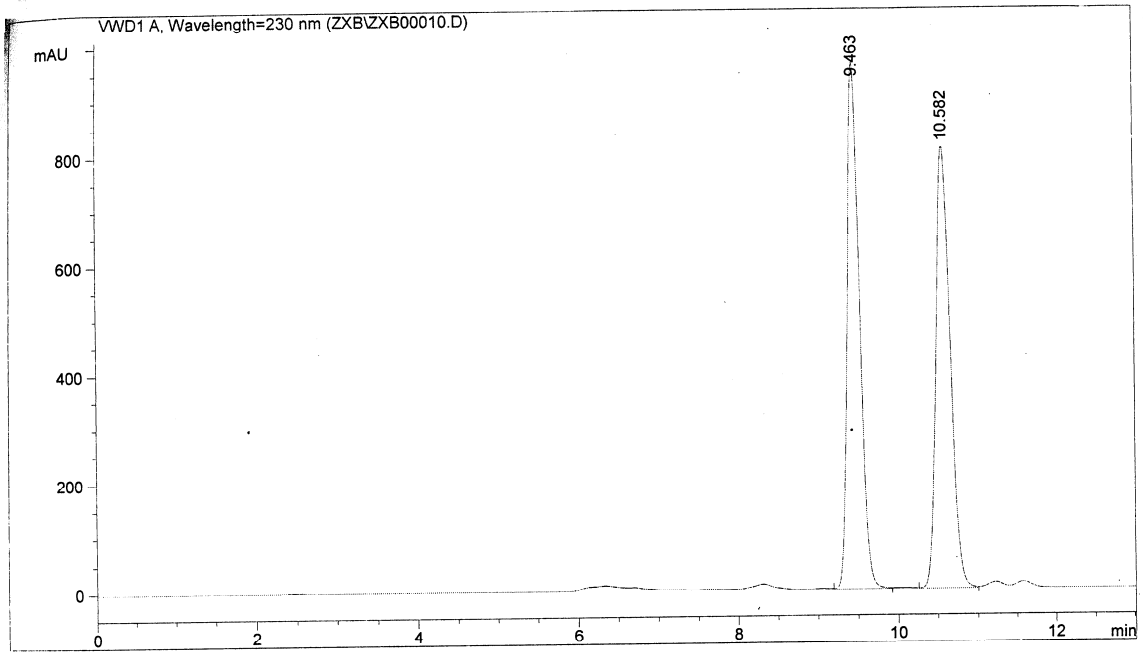

13.800
21.168
21.899
28.732
29.692
31.757
76.575
76.870
77.000
77.423
95.878
127.481
128.028
128.130
144.436
149.307
Ph
C_5H_{11}-*n*
HO
I
(S)-Z-**4a**
zxb-1-144-c
0
20
40
60
80
100
120
140
160
180

e/i-propanol=95/5; 230nm; 0.5 ml/min; AS-H

```
tion Date  : 4/24/2008 7:55:08 PM
e Name     : zxb-1-I44 90                    Location
Operator   : zxb
Method     : D:\HPCHEM\1\METHODS\ERIC.M
t changed  : 4/24/2008 7:53:31 PM by zxb
             (modified after loading)
alysis Method : D:\HPCHEM\1\METHODS\ERIC.M
st changed    : 4/24/2008 8:44:47 PM by mao
             (modified after loading)
```



Z-4a



Area Percent Report

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


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.463 VV    0.1632 1.01411e4   966.16229  50.0983
   2  10.582 VV    0.1934 1.01013e4   810.89063  49.9017

Totals :                  2.02423e4  1777.05292

 Results obtained with enhanced integrator!
```

*** End of Report ***

Hexane/i-propanol=95/5; 230nm; 0.5 ml/min; AS-H

```
Injection Date   : 4/24/2008 8:23:09 PM
Sample Name      : zxb-1-144                          Location :  -
Acq. Operator    : zxb
Acq. Method      : D:\HPCHEM\1\METHODS\ERIC.M
Last changed     : 4/24/2008 7:53:31 PM by zxb
                   (modified after loading)
Analysis Method  : D:\HPCHEM\1\METHODS\ERIC.M
Last changed     : 4/24/2008 8:44:47 PM by mao
                   (modified after loading)
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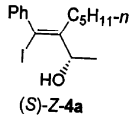
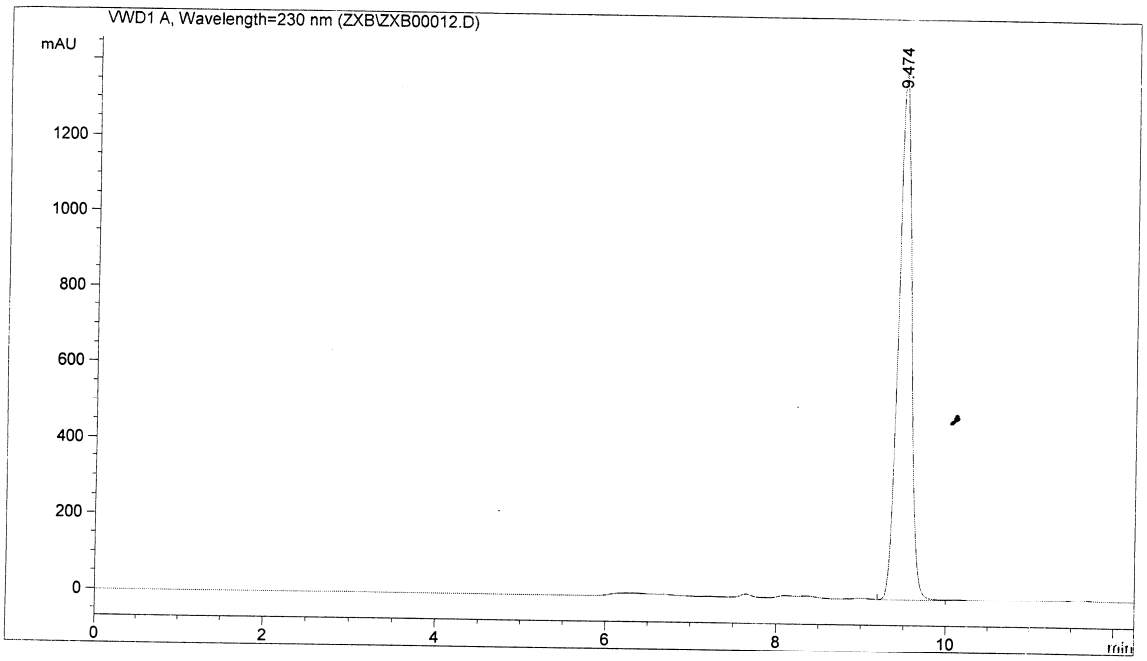


(*S*)-Z-4a




```
                        Area Percent Report

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

Signal 1: VWD1 A, Wavelength=230 nm

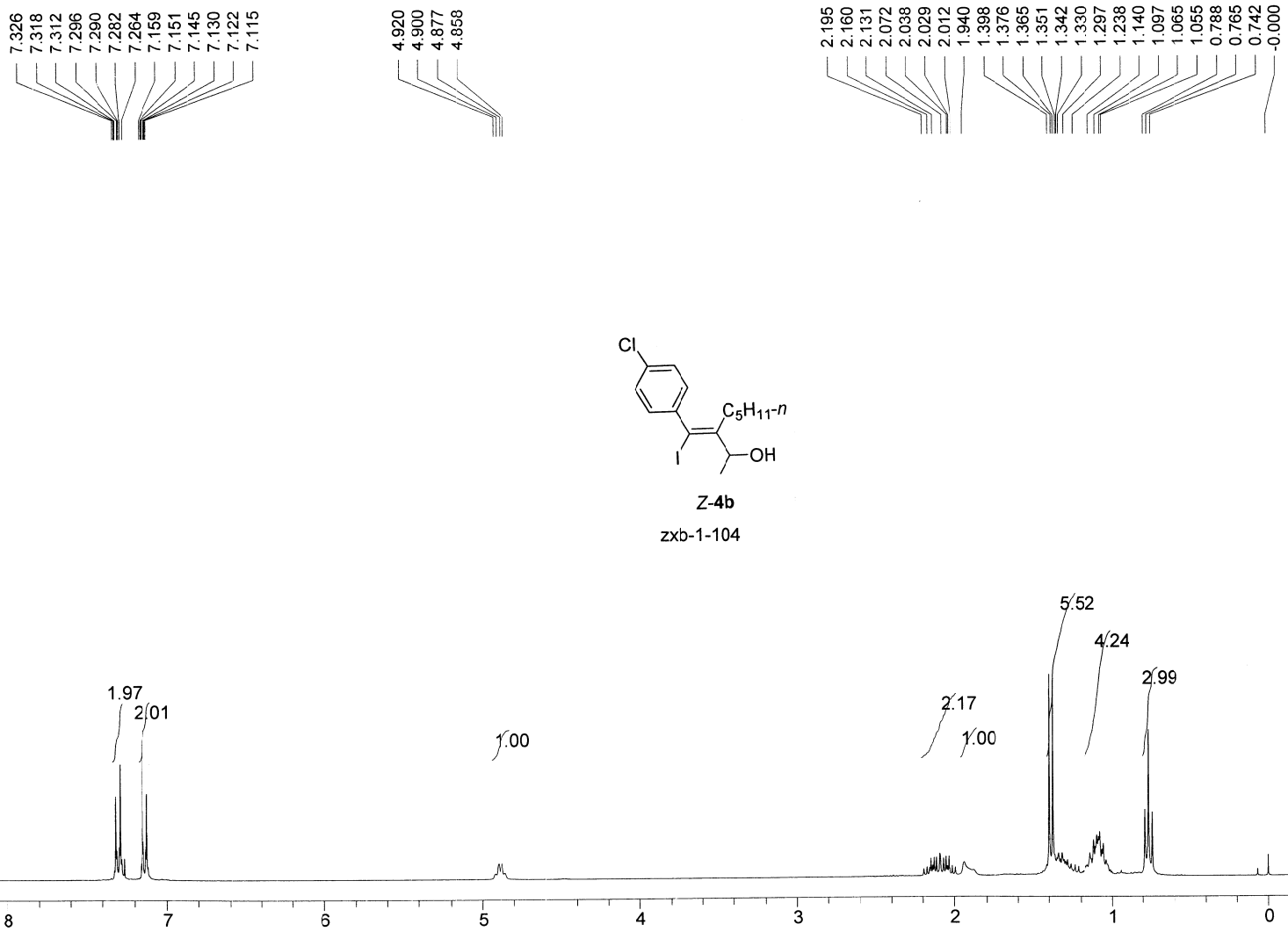
Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]  mAU   *s    [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1   9.474 VV    0.1640 1.46850e4  1390.35144 100.0000

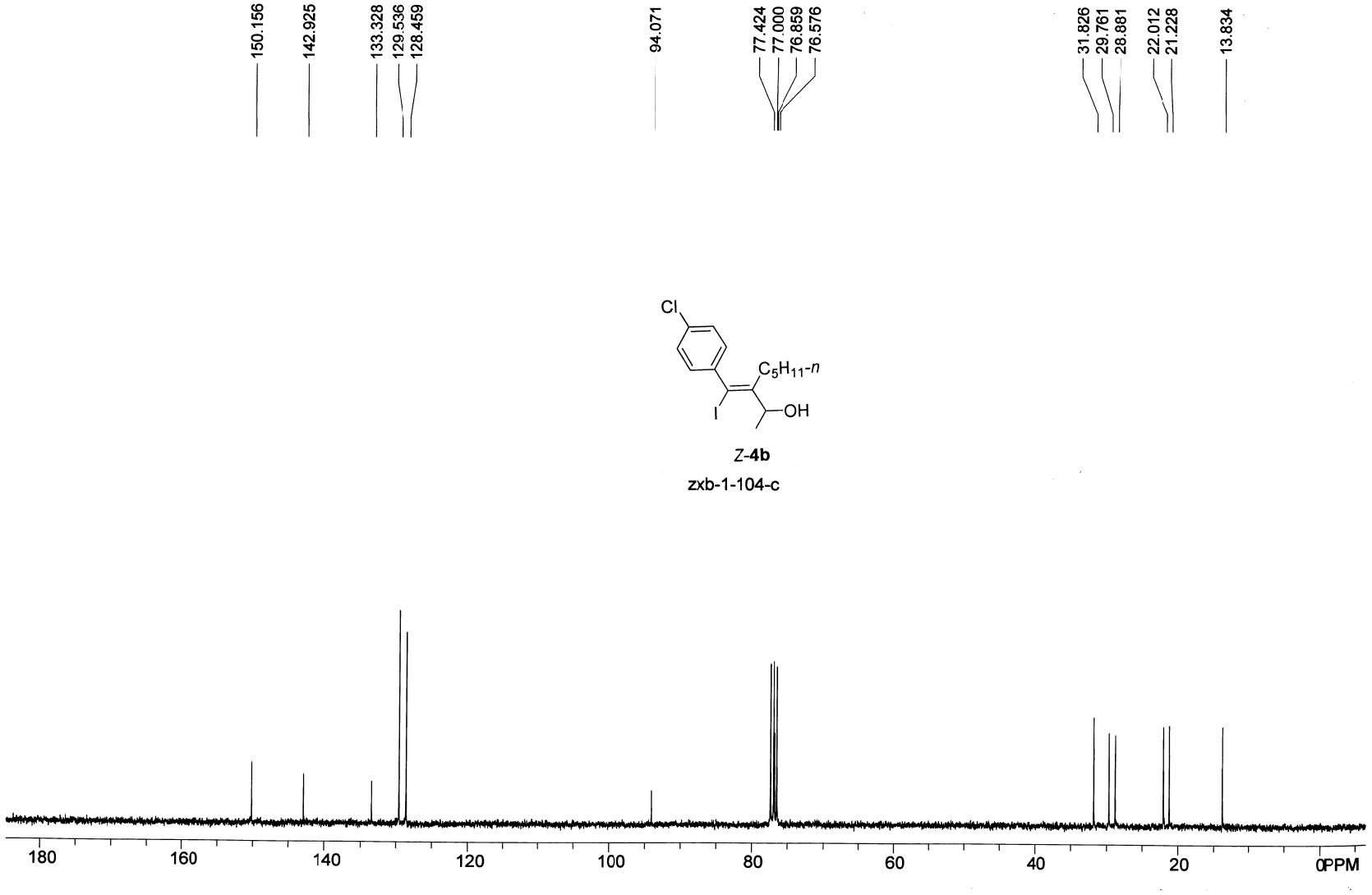
Totals :                  1.46850e4  1390.35144

 Results obtained with enhanced integrator!

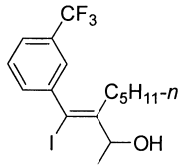
                        *** End of Report ***
```

rument 1 4/24/2008 9:11:41 PM mao


7.326
7.318
7.312
7.296
7.290
7.282
7.264
7.159
7.151
7.145
7.130
7.122
7.115
4.920
4.900
4.877
4.858
2.195
2.160
2.131
2.072
2.038
2.029
2.012
1.940
1.398
1.376
1.365
1.351
1.342
1.330
1.297
1.238
1.140
1.097
1.065
1.055
0.788
0.765
0.742
-0.000
Cl
C5H11-n
I
OH
Z-4b
zxb-1-104
1.97
2.01
1.00
2.17
1.00
5.52
4.24
2.99
8
7
6
5
4
3
2
1
0
PPM

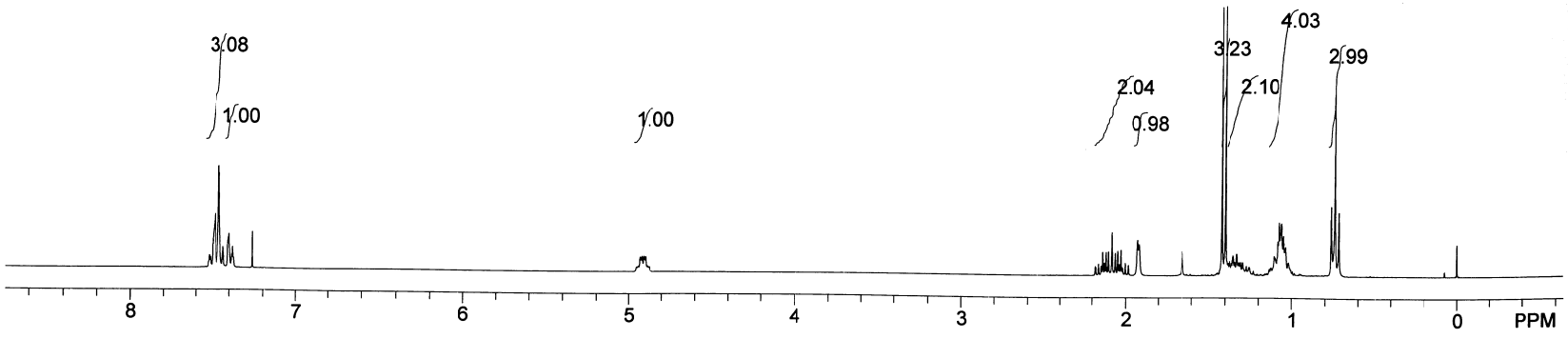

150.156
142.925
133.328
129.536
128.459
94.071
77.424
77.000
76.859
76.576
31.826
29.761
28.881
22.012
21.228
13.834
Cl
C_5H_{11}-*n*
I
OH
Z-4b
zxb-1-104-c
180
160
140
120
100
80
60
40
20
0PPM

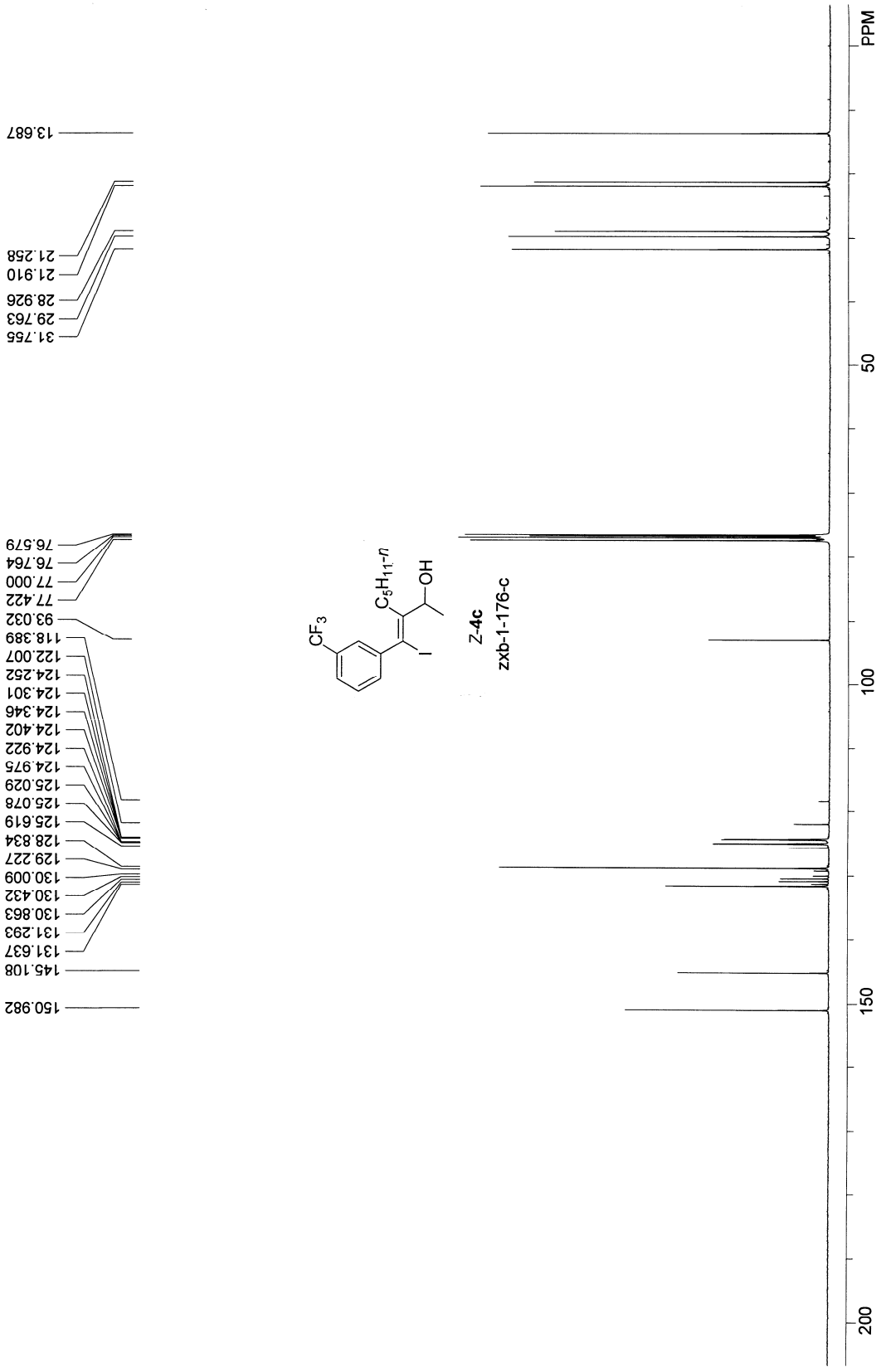

7.522
7.501
7.488
7.464
7.438
7.402
7.385
7.264
4.954
4.943
4.933
4.921
4.910
4.900
4.889
4.878
2.181
2.137
2.117
2.102
2.082
2.038
2.019
1.984
1.925
1.914
1.419
1.397
1.348
1.337
1.325
1.304
1.252
1.229
1.137
1.097
1.072
1.058
1.035
1.018
0.759
0.736
0.713
0.000

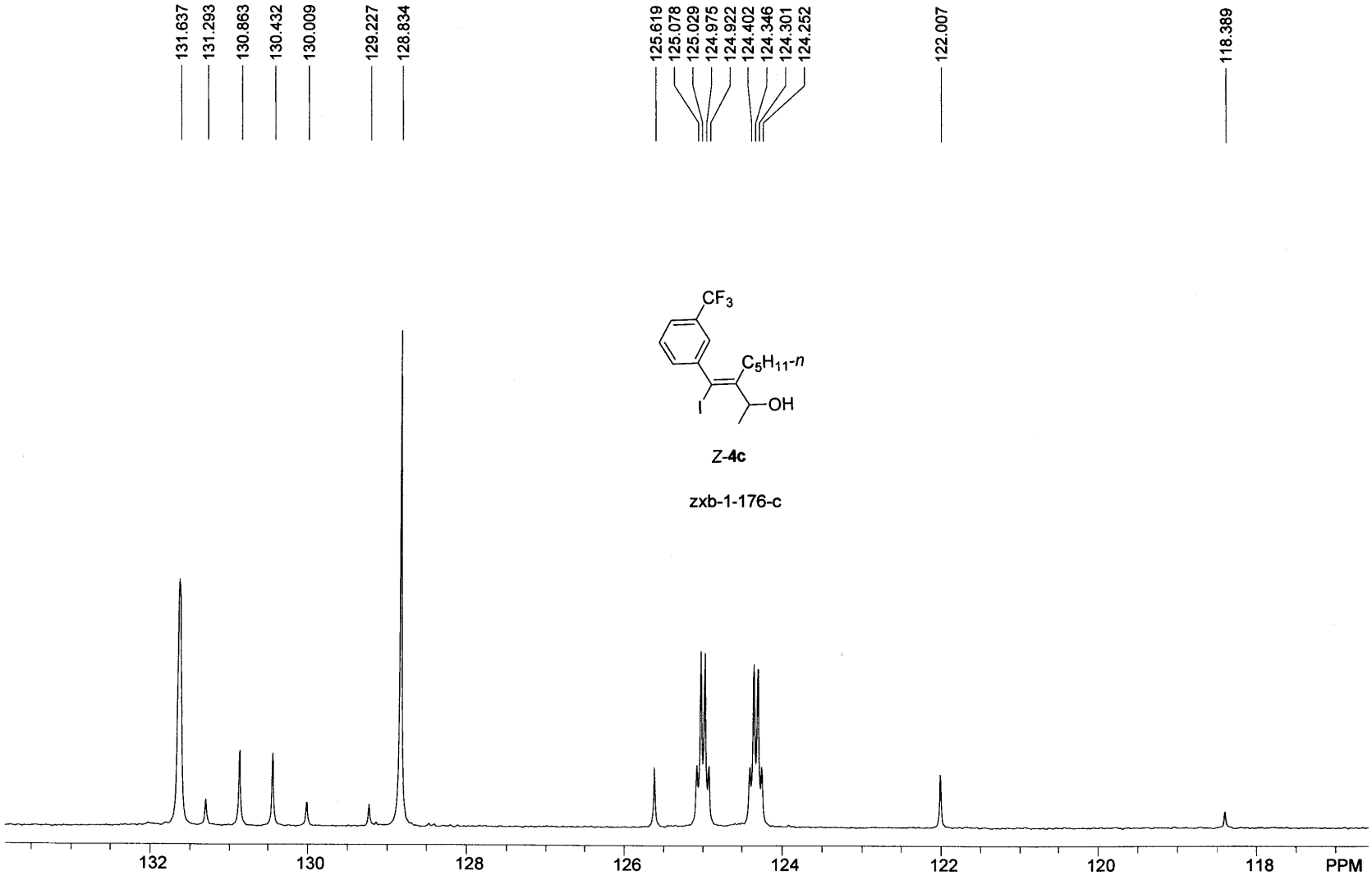

CF3
C5H11-n
I
OH

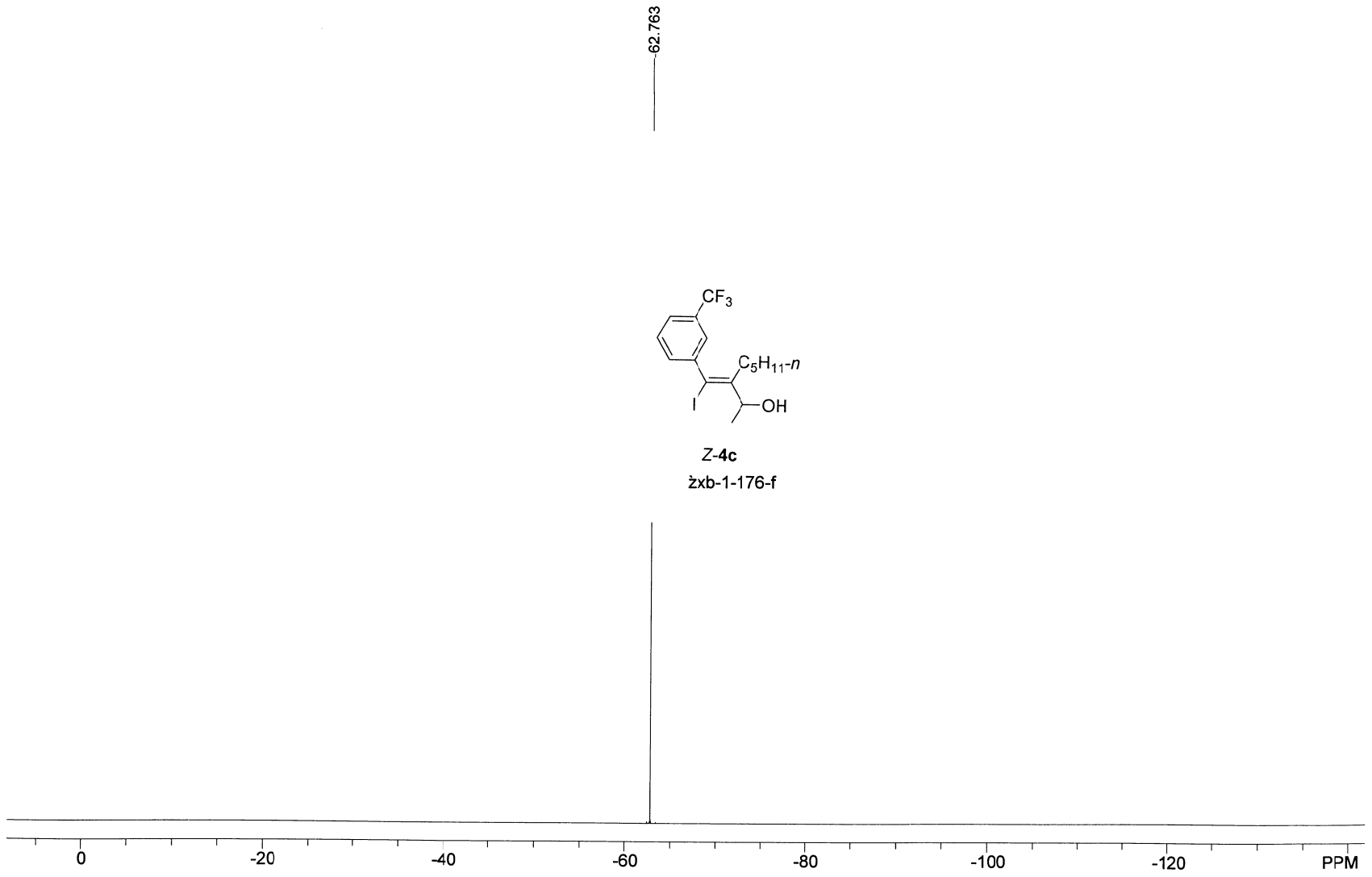
Z-**4c**

zxb-1-176


3.08
1.00
1.00
2.04
0.98
3.23
2.10
4.03
2.99
8
7
6
5
4
3
2
1
0
PPM

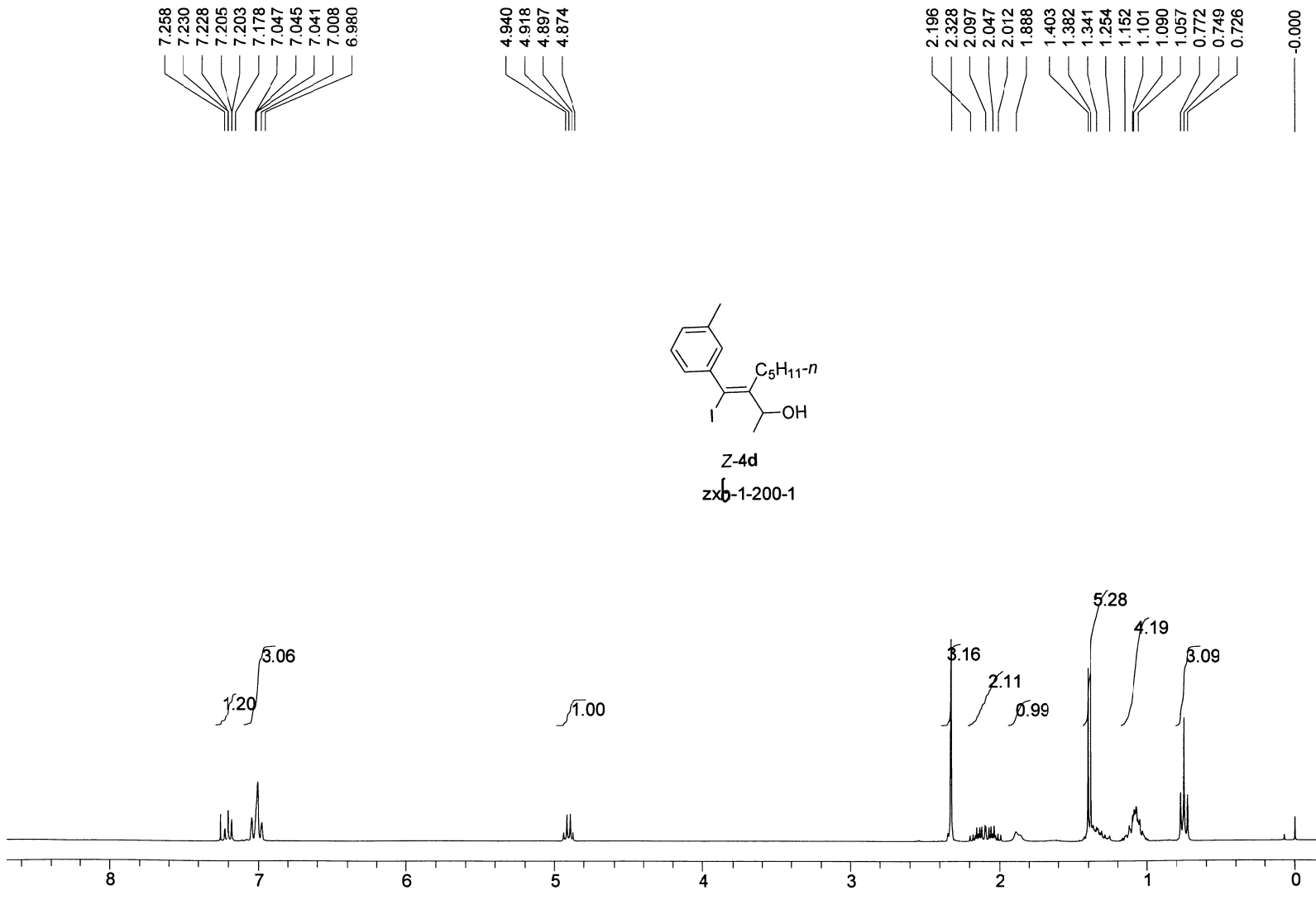

13.687
21.258
21.910
28.926
29.763
31.755
76.579
76.764
77.000
77.422
93.032
118.389
122.007
124.252
124.301
124.346
124.402
124.922
124.975
125.029
125.078
125.619
128.834
129.227
130.009
130.432
130.863
131.293
131.637
145.108
150.982
CF3
C5H11-n
OH
I
Z-4c
zxb-1-176-c
PPM
50
100
150
200

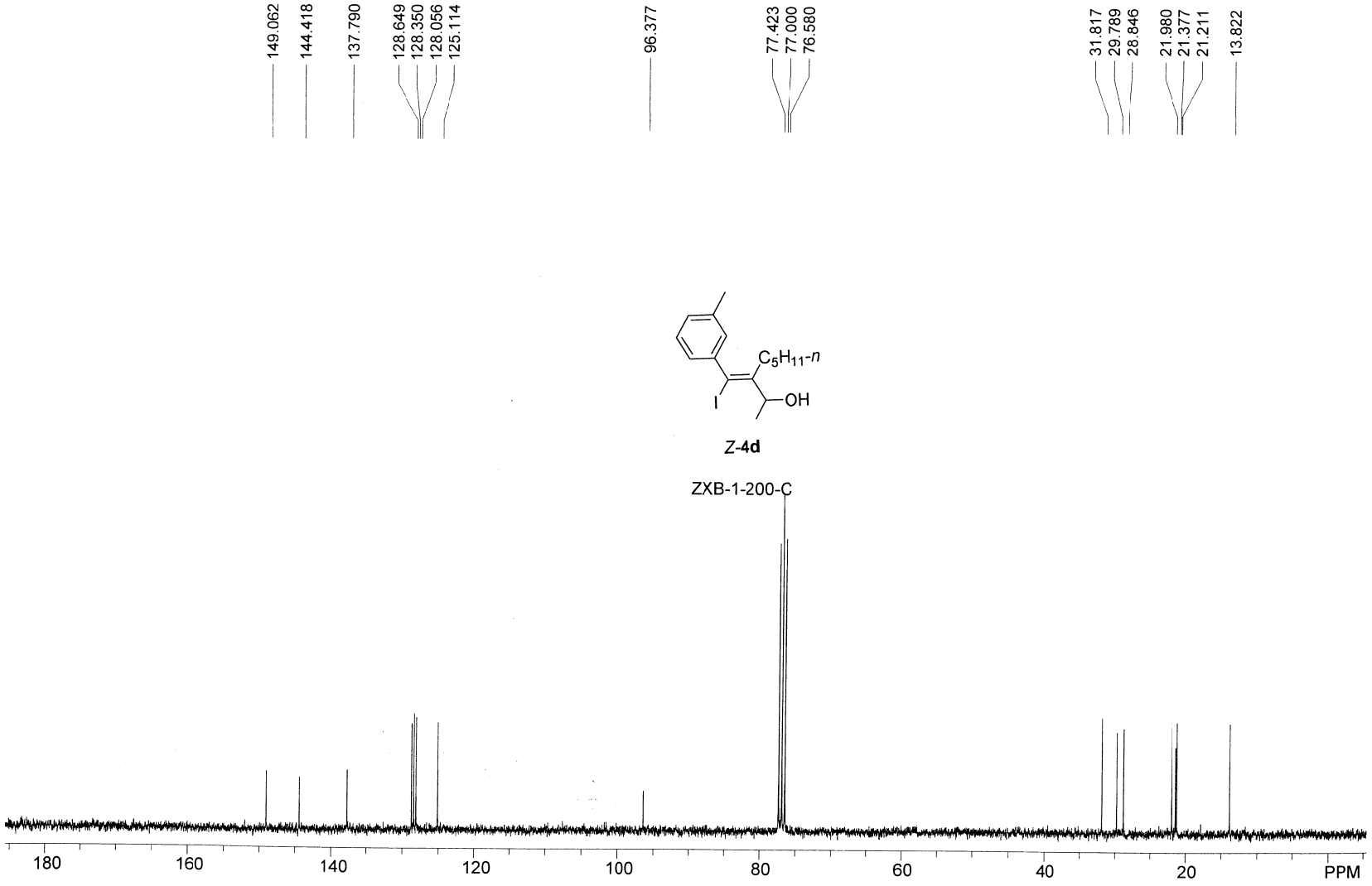

131.637
131.293
130.863
130.432
130.009
129.227
128.834
125.619
125.078
125.029
124.975
124.922
124.402
124.346
124.301
124.252
122.007
118.389
CF3
C5H11-n
I
OH
Z-4c
zxb-1-176-c
132
130
128
126
124
122
120
118
PPM

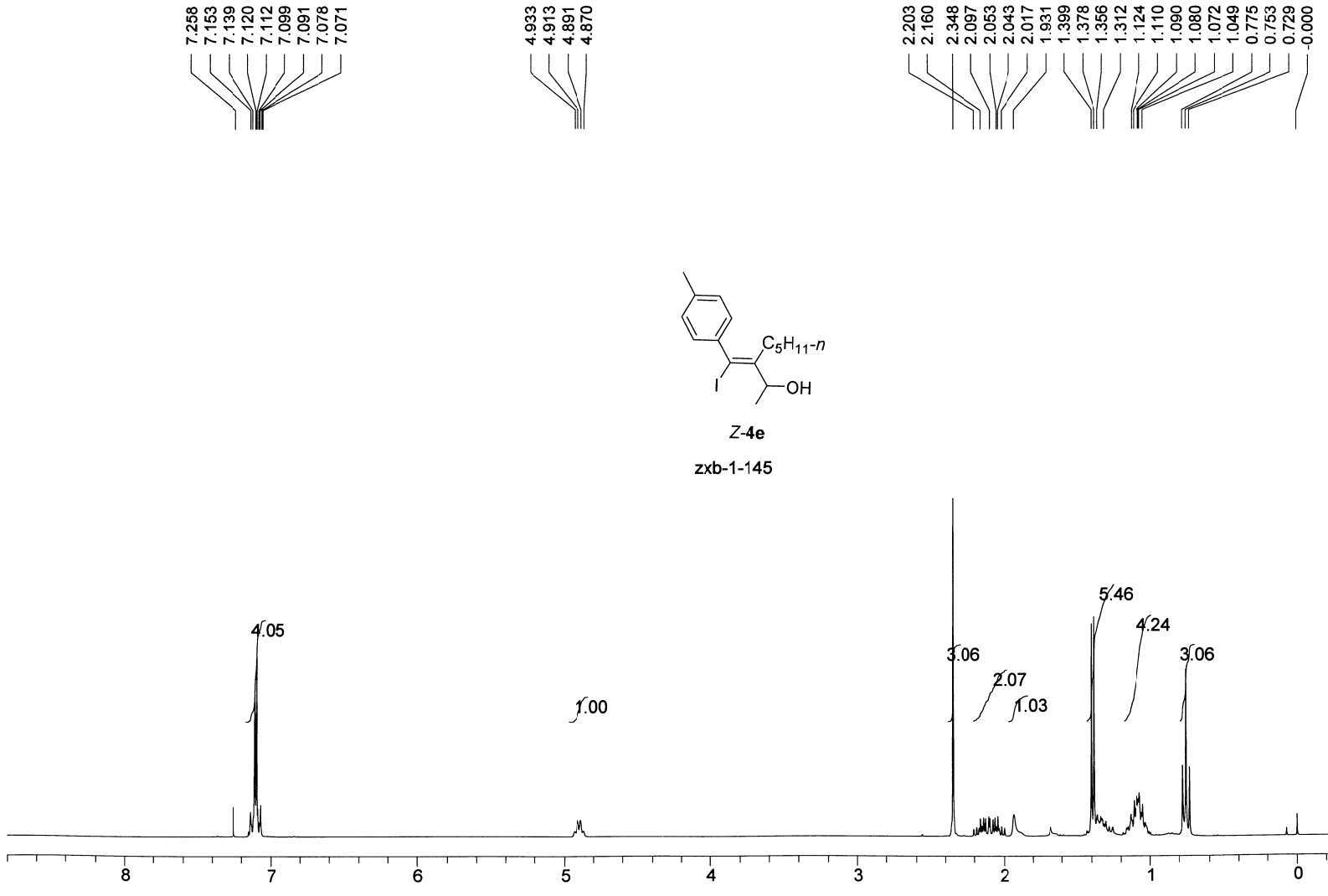


Z-**4c**

żxb-1-176-f


7.258
7.230
7.228
7.205
7.203
7.178
7.047
7.045
7.041
7.008
6.980
4.940
4.918
4.897
4.874
2.196
2.328
2.097
2.047
2.012
1.888
1.403
1.382
1.341
1.254
1.152
1.101
1.090
1.057
0.772
0.749
0.726
-0.000
C5H11-n
I
OH
Z-4d
zxb-1-200-1
3.06
1.20
1.00
3.16
2.11
0.99
5.28
4.19
3.09
8
7
6
5
4
3
2
1
0
PPM


149.062
144.418
137.790
128.649
128.350
128.056
125.114
96.377
77.423
77.000
76.580
31.817
29.789
28.846
21.980
21.377
21.211
13.822
C_5H_{11}-*n*
I
OH
Z-**4d**
ZXB-1-200-C
180
160
140
120
100
80
60
40
20
PPM


7.258
7.153
7.139
7.120
7.112
7.099
7.091
7.078
7.071
4.933
4.913
4.891
4.870
2.203
2.160
2.348
2.097
2.053
2.043
2.017
1.931
1.399
1.378
1.356
1.312
1.124
1.110
1.090
1.080
1.072
1.049
0.775
0.753
0.729
-0.000
C5H11-n
I
OH
Z-4e
zxb-1-145
4.05
1.00
3.06
2.07
1.03
5.46
4.24
3.06
8
7
6
5
4
3
2
1
0
PPM

13.812
21.197
22.013
28.838
29.762
31.840
76.677
77.000
77.050
77.324
96.540
127.984
128.851
137.318
141.781
149.115
C5H11-n
OH
I
Z-4e
lz-5-12-c
0 PPM
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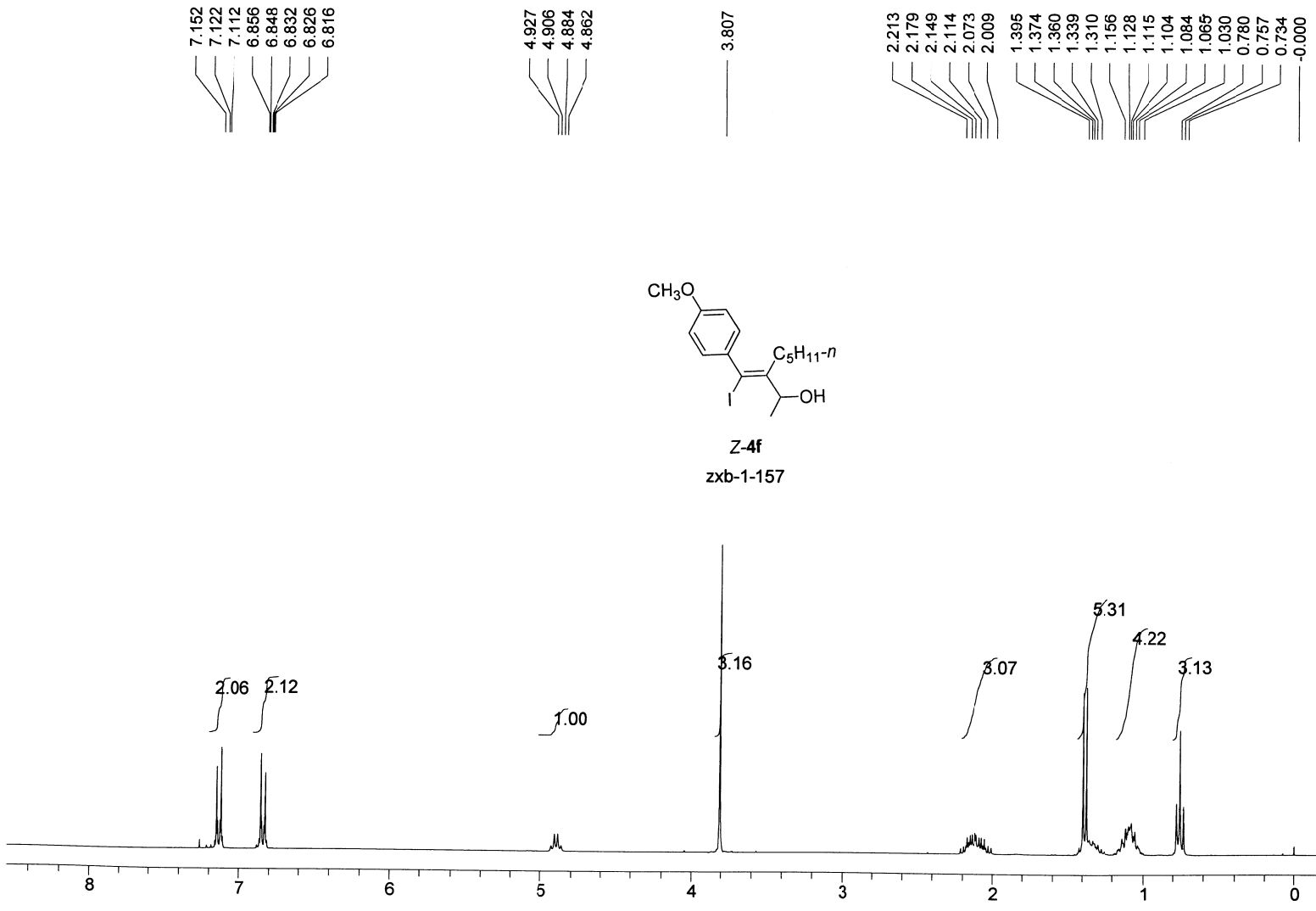
60
80
100
120
140
160
180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7.122
7.112
6.856
6.848
6.832
6.826
6.816
4.927
4.906
4.884
4.862
3.807
2.213
2.179
2.149
2.114
2.073
2.009
1.395
1.374
1.360
1.339
1.310
1.156
1.128
1.115
1.104
1.084
1.065
1.030
0.780
0.757
0.734
-0.000
CH3O
C5H11-n
I
OH
Z-4f
zxb-1-157
2.06
2.12
1.00
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3.07
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3.13
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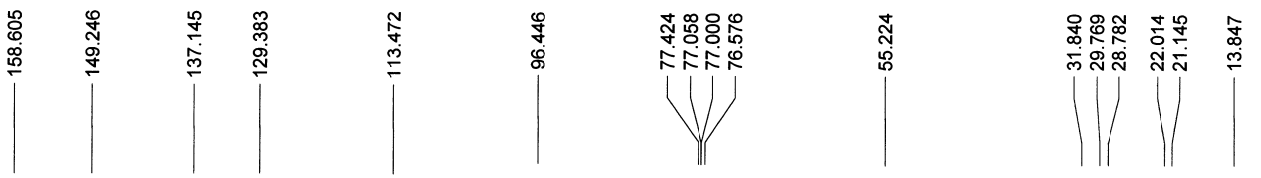
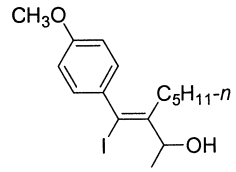
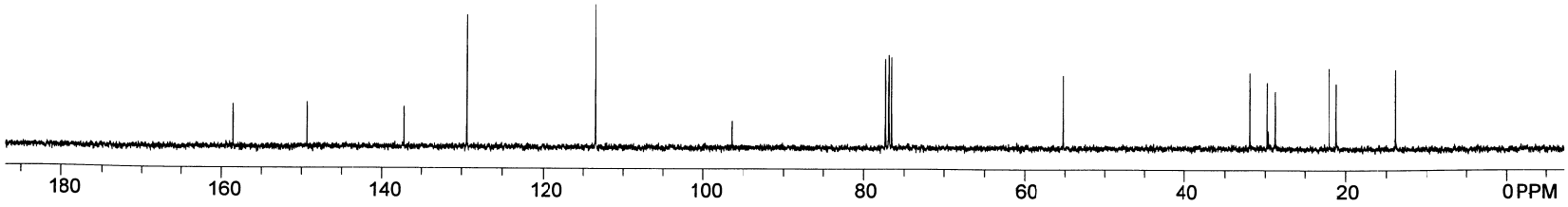
PPM





Z-**4f**

zxb-1-157-c

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7.307
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7.183
7.179
4.746
4.724
4.702
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2.147
2.122
2.082
2.043
2.018
1.963
1.677
1.655
1.614
1.425
1.385
1.372
1.327
1.315
1.259
1.235
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1.038
1.030
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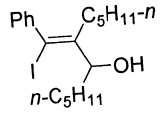
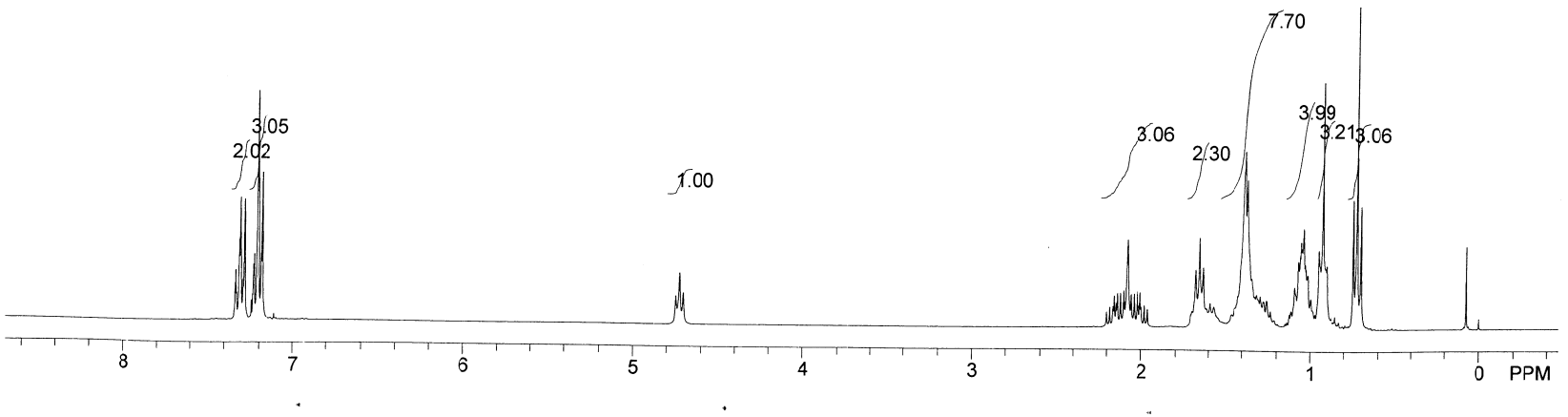
0.950
0.927
0.903
0.746
0.723
0.700


Ph
C5H11-n
I
OH
n-C5H11

Z-**4g**

zxb-1-103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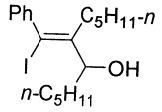
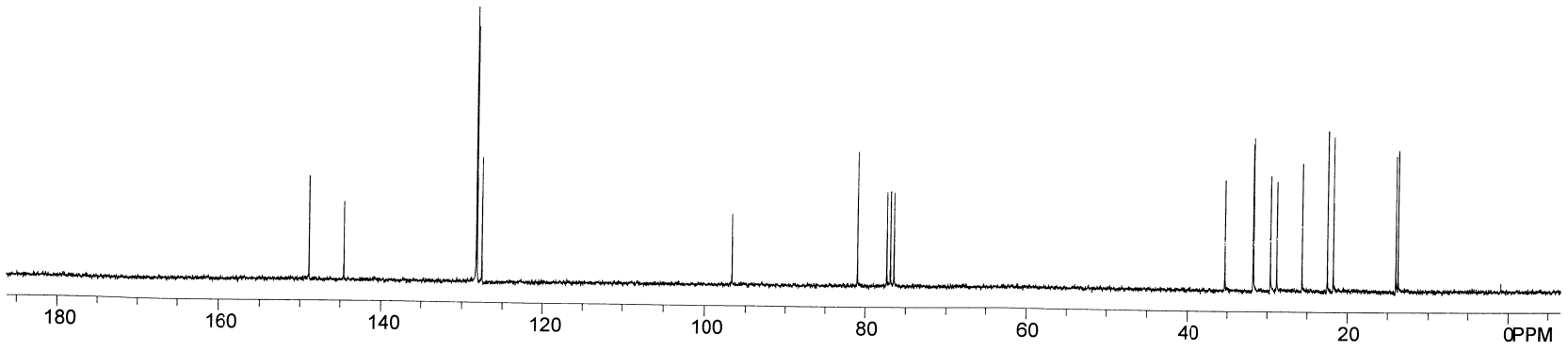
1.00
3.06
2.30
7.70
3.99
3.21
3.06
8
7
6
5
4
3
2
1
0
PPM

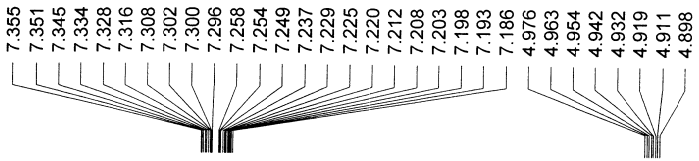
148.909
144.584
128.139
128.042
127.463
96.654
80.947
77.424
77.000
76.575
35.334
31.803
31.725
29.685
28.932
25.713
22.611
21.890
14.062
13.793



Z-**4g**

zxb-1-103-c

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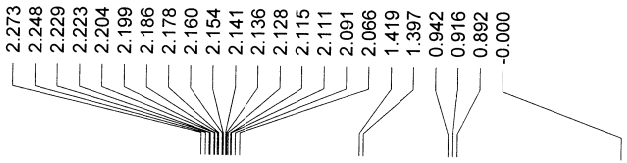
7.345
7.334
7.328
7.316
7.308
7.302
7.300
7.296
7.258
7.254
7.249
7.237
7.229
7.225
7.220
7.212
7.208
7.203
7.198
7.193
7.186
4.976
4.963
4.954
4.942
4.932
4.919
4.911
4.898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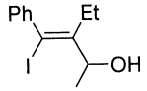
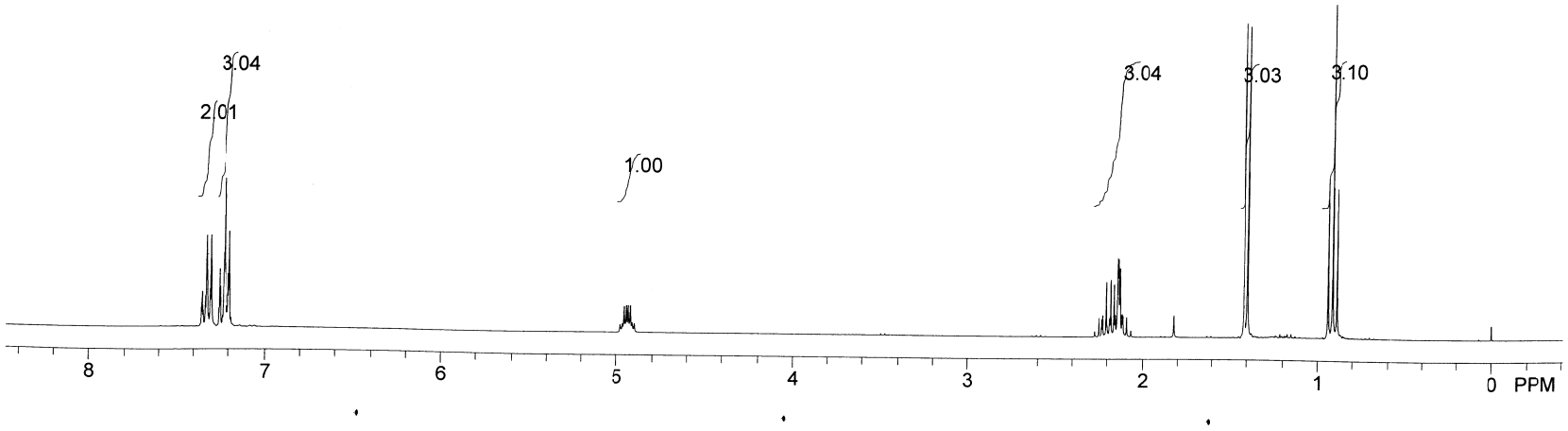
2.248
2.229
2.223
2.204
2.199
2.186
2.178
2.160
2.154
2.141
2.136
2.128
2.115
2.111
2.091
2.066
1.419
1.397
0.942
0.916
0.892
-0.000


Ph
Et
I
OH

***Z*-4h**

ZXB-1-93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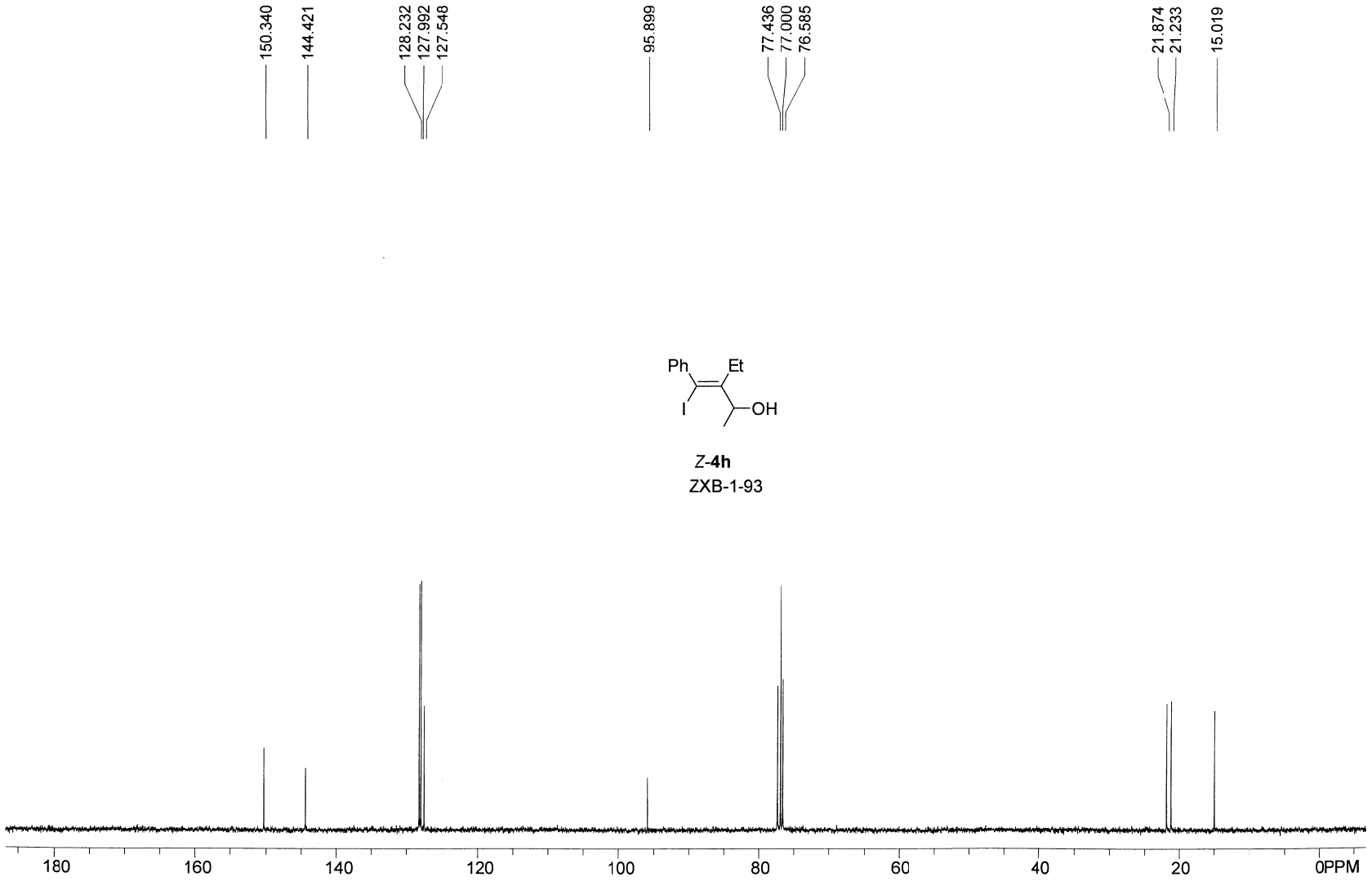
2.01
1.00
3.04
3.03
3.10
8
7
6
5
4
3
2
1
0
PPM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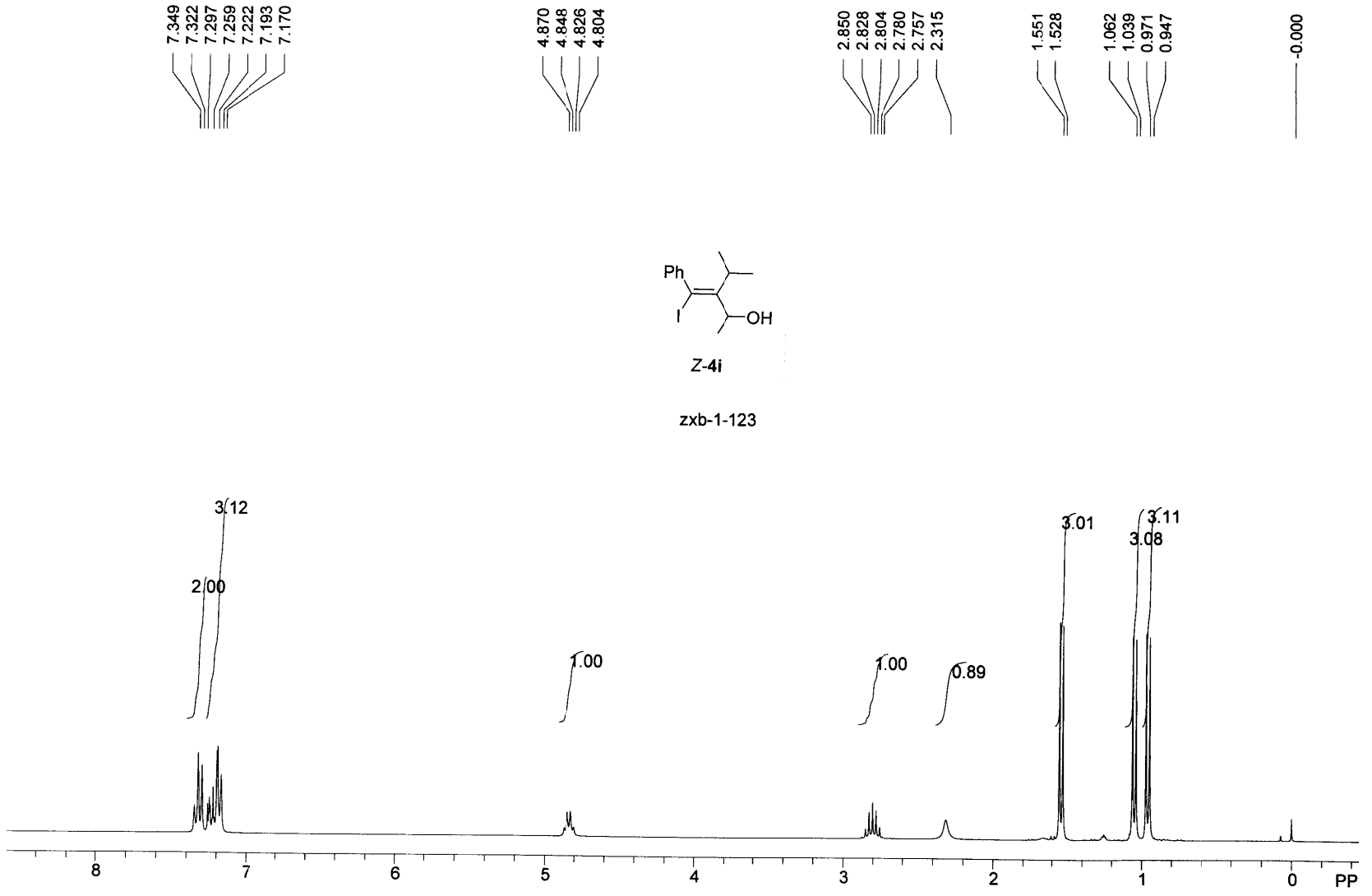
144.421
128.232
127.992
127.548
95.899
77.436
77.000
76.585
21.874
21.233
15.019
Ph
Et
I
OH
Z-4h
ZXB-1-93
180
160
140
120
100
80
60
40
20
0PPM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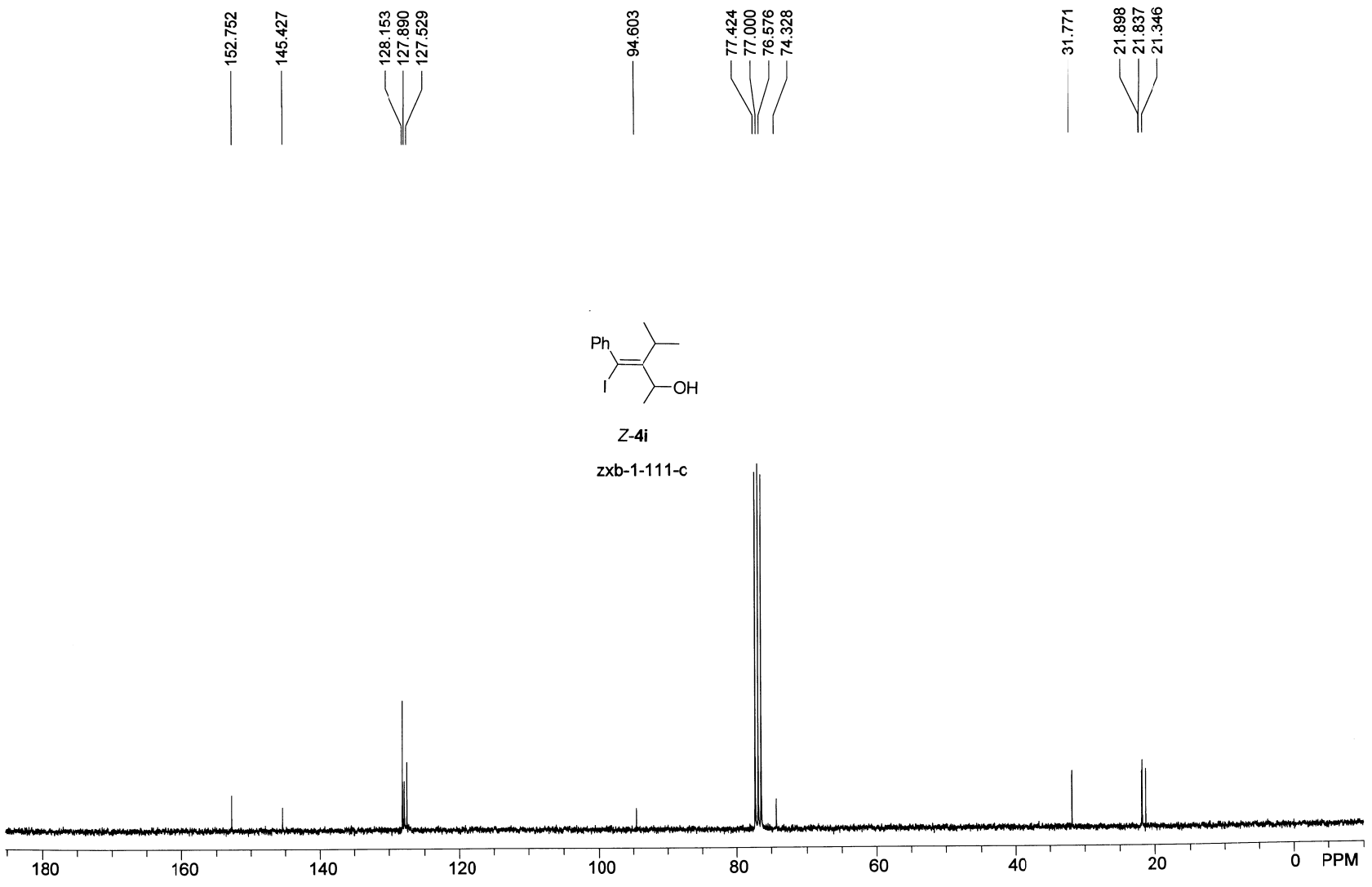
7.297
7.259
7.222
7.193
7.170
4.870
4.848
4.826
4.804
2.850
2.828
2.804
2.780
2.757
2.315
1.551
1.528
1.062
1.039
0.971
0.947
-0.000
Ph
I
OH
Z-4i
zxb-1-123
3.12
2.00
1.00
1.00
0.89
3.01
3.11
3.08
8
7
6
5
4
3
2
1
0
PP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128.153
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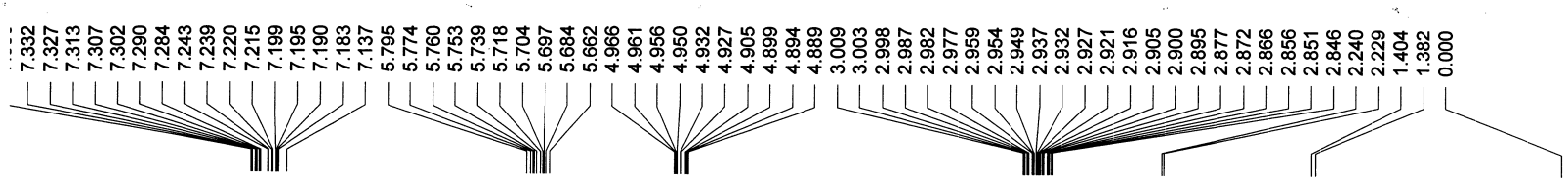
127.529
94.603
77.424
77.000
76.576
74.328
31.771
21.898
21.837
21.346
Ph
I
OH
Z-4i
zxb-1-111-c
180
160
140
120
100
80
60
40
20
0
PPM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7.327
7.313
7.307
7.302
7.290
7.284
7.243
7.239
7.220
7.215
7.199
7.195
7.190
7.183
7.137
5.795
5.774
5.760
5.753
5.739
5.718
5.704
5.697
5.684
5.662
4.966
4.961
4.956
4.950
4.932
4.927
4.905
4.899
4.894
4.889
3.009
3.003
2.998
2.987
2.982
2.977
2.959
2.954
2.949
2.937
2.932
2.927
2.921
2.916
2.905
2.900
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2.872
2.866
2.856
2.851
2.846
2.240
2.229
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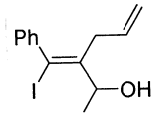
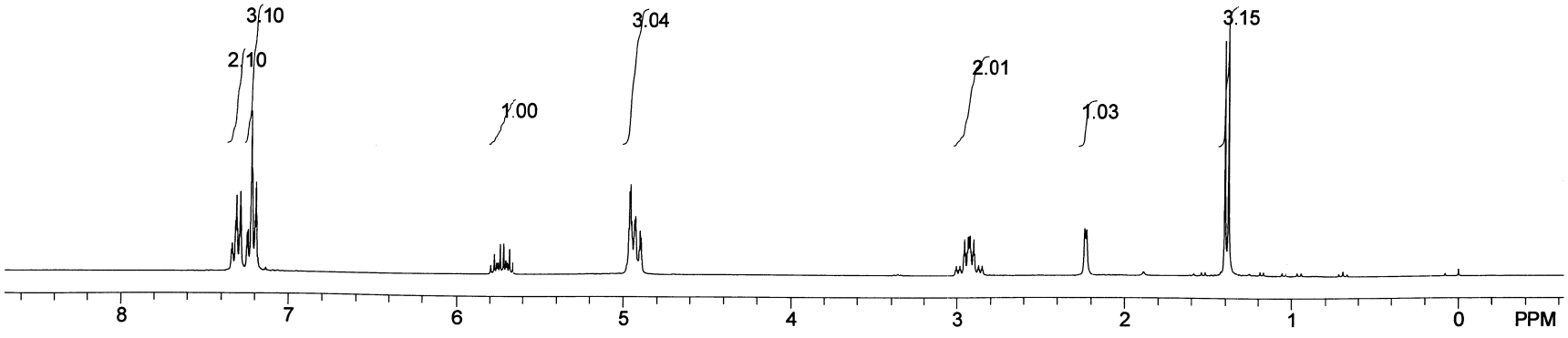
1.382
0.000

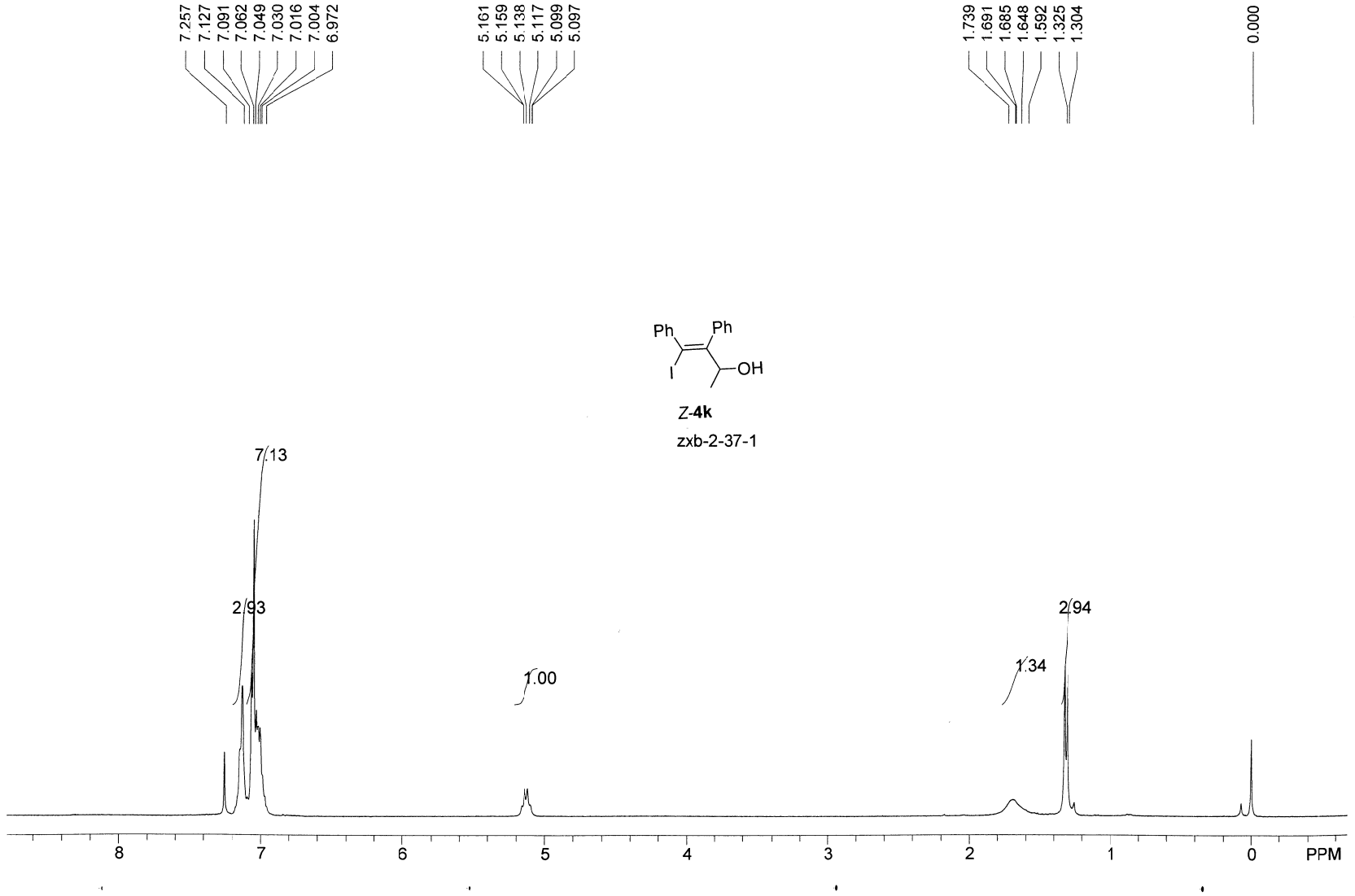

Ph
I
OH

Z-**4j**

ZXB-1-84


3.10
2.10
1.00
3.04
2.01
1.03
3.15
8
7
6
5
4
3
2
1
0
PPM

21.170
32.802
76.581
77.000
77.424
96.996
116.051
127.780
128.047
128.225
137.010
144.091
146.201
Ph
I
OH
Z-4j
zxb-1-84-c
PPM
20
40
60
80
100
120
140
160
180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7.091
7.062
7.049
7.030
7.016
7.004
6.972
5.161
5.159
5.138
5.117
5.099
5.097
1.739
1.691
1.685
1.648
1.592
1.325
1.304
0.000
Ph
Ph
I
OH
Z-4k
zxb-2-37-1
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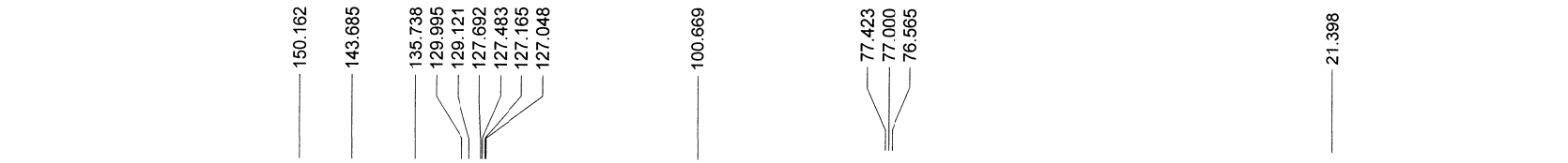
2.93
1.00
1.34
2.94
8
7
6
5
4
3
2
1
0
PPM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127.483
127.165
127.048
100.669
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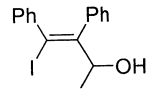
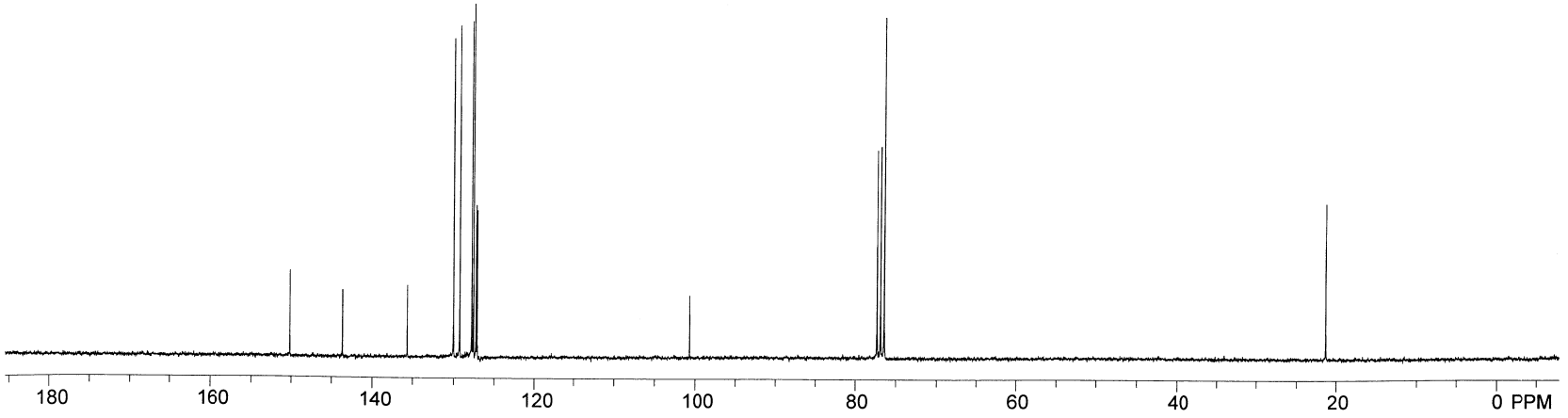
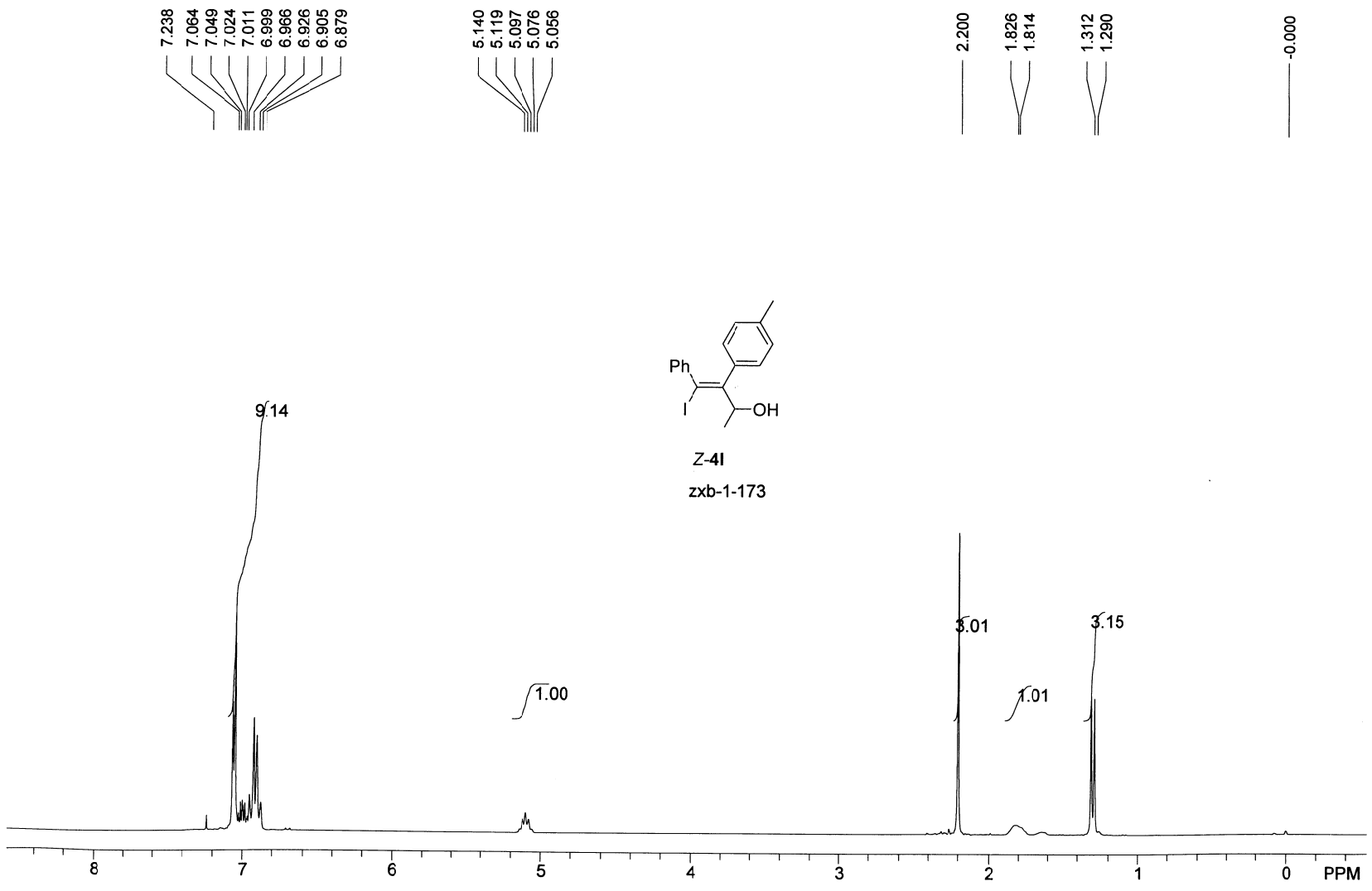
77.000
76.565
21.398


Ph
Ph
I
OH

Z-**4k**

zxb-1-86-c


180
160
140
120
100
80
60
40
20
0 PPM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7.024
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6.966
6.926
6.905
6.879
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5.119
5.097
5.076
5.056
2.200
1.826
1.814
1.312
1.290
-0.000
Ph
I
OH
Z-4l
zxb-1-173
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1.01
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6
5
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2
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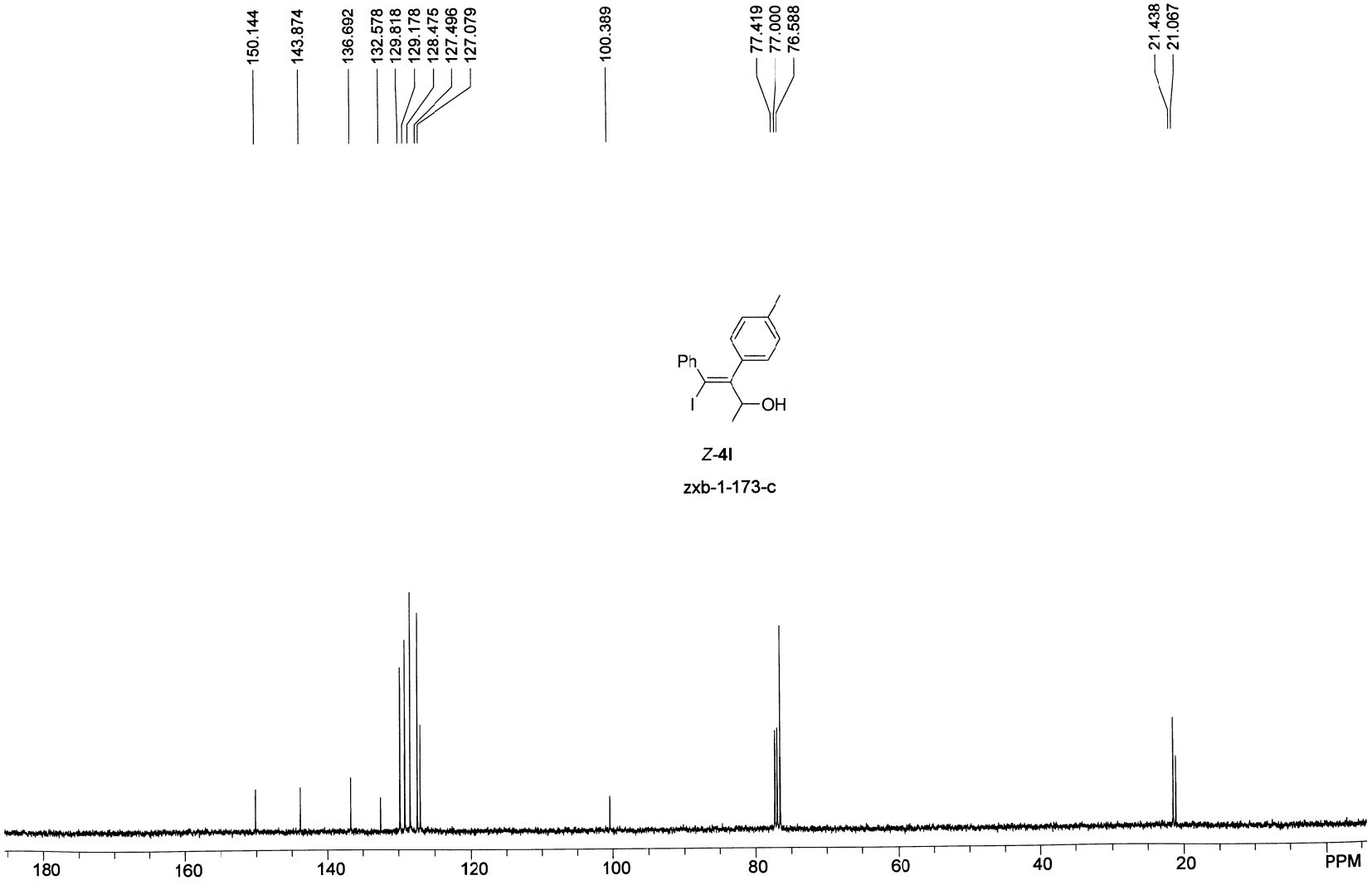
0
PPM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77.000
76.588
21.438
21.067
Ph
I
OH
Z-4l
zxb-1-173-c
180
160
140
120
100
80
60
40
20
PPM


7.255
7.100
7.095
7.075
7.072
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7.054
7.021
7.015
6.983
6.973
6.958
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6.910
6.695
6.687
6.680
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6.657
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5.109
5.088
5.066
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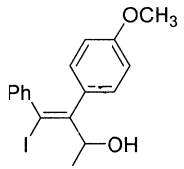
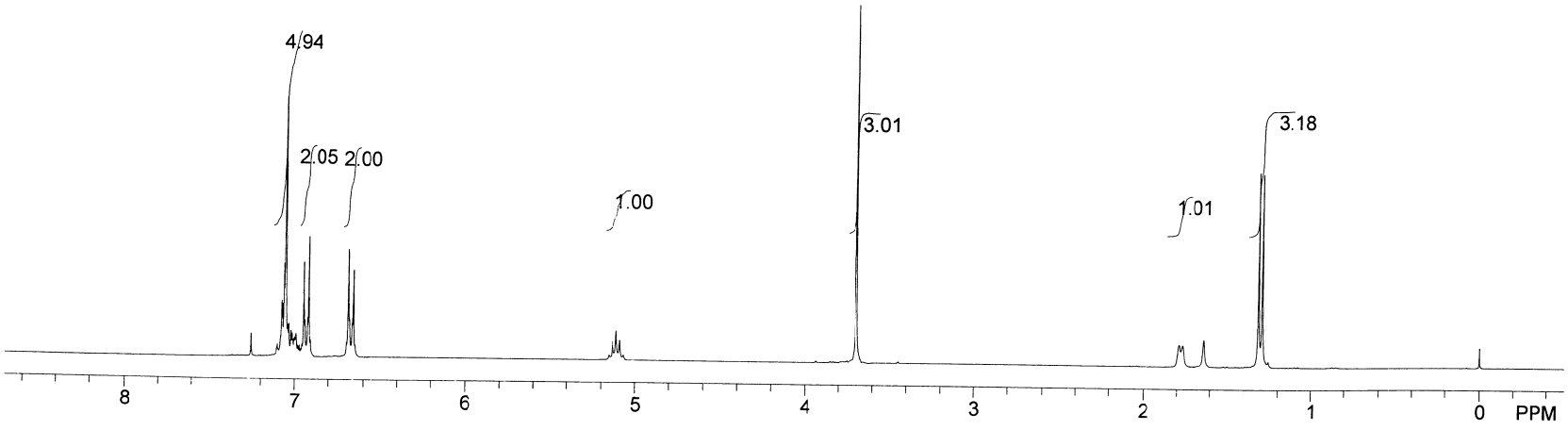
1.290
-0.000


OCH3
Ph
I
OH

Z-4m

zxb-2-10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1.01
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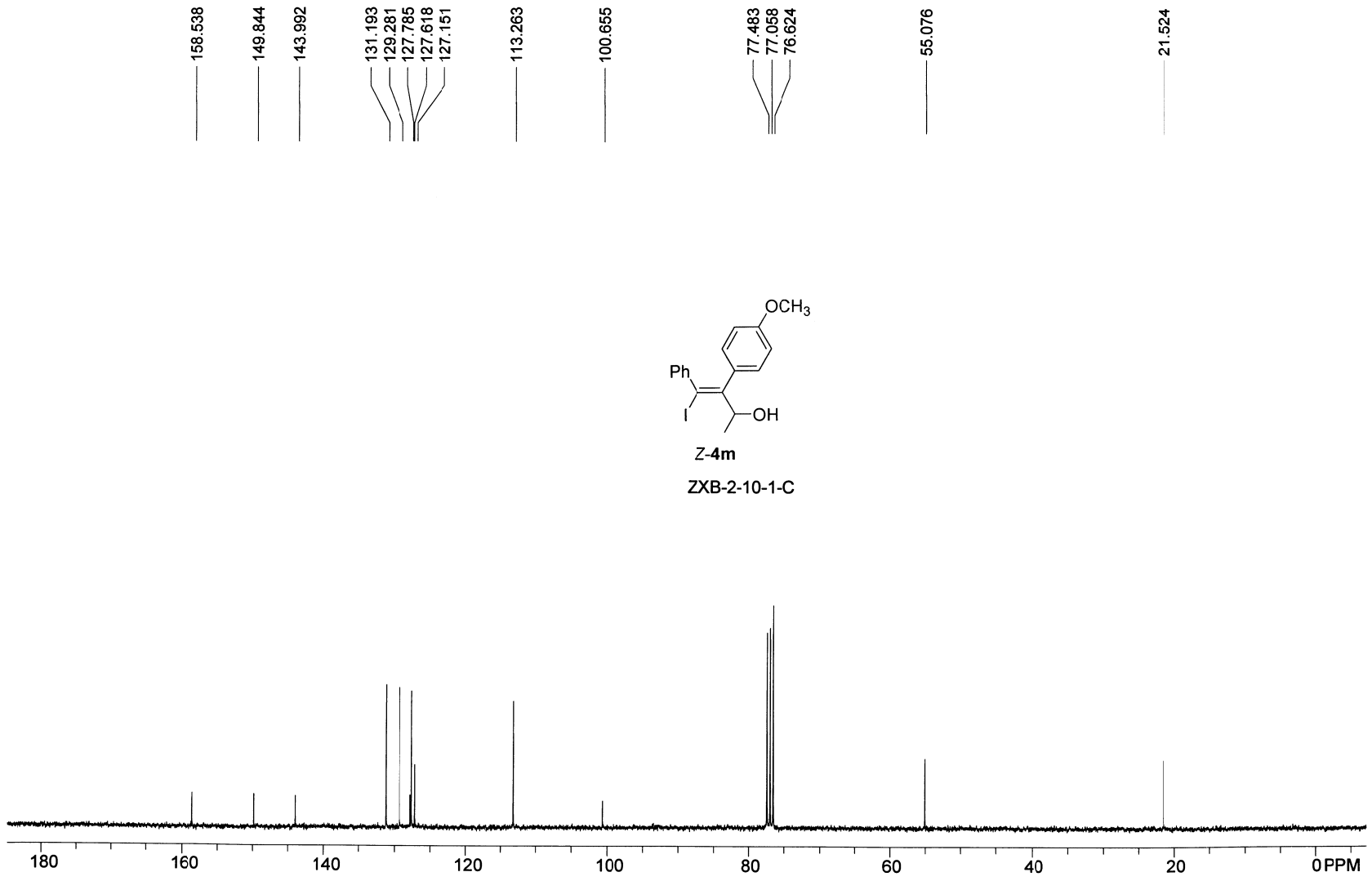
8
7
6
5
4
3
2
1
0
PPM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127.151
113.263
100.655
77.483
77.058
76.624
55.076
21.524
OCH3
Ph
I
OH
Z-4m
ZXB-2-10-1-C
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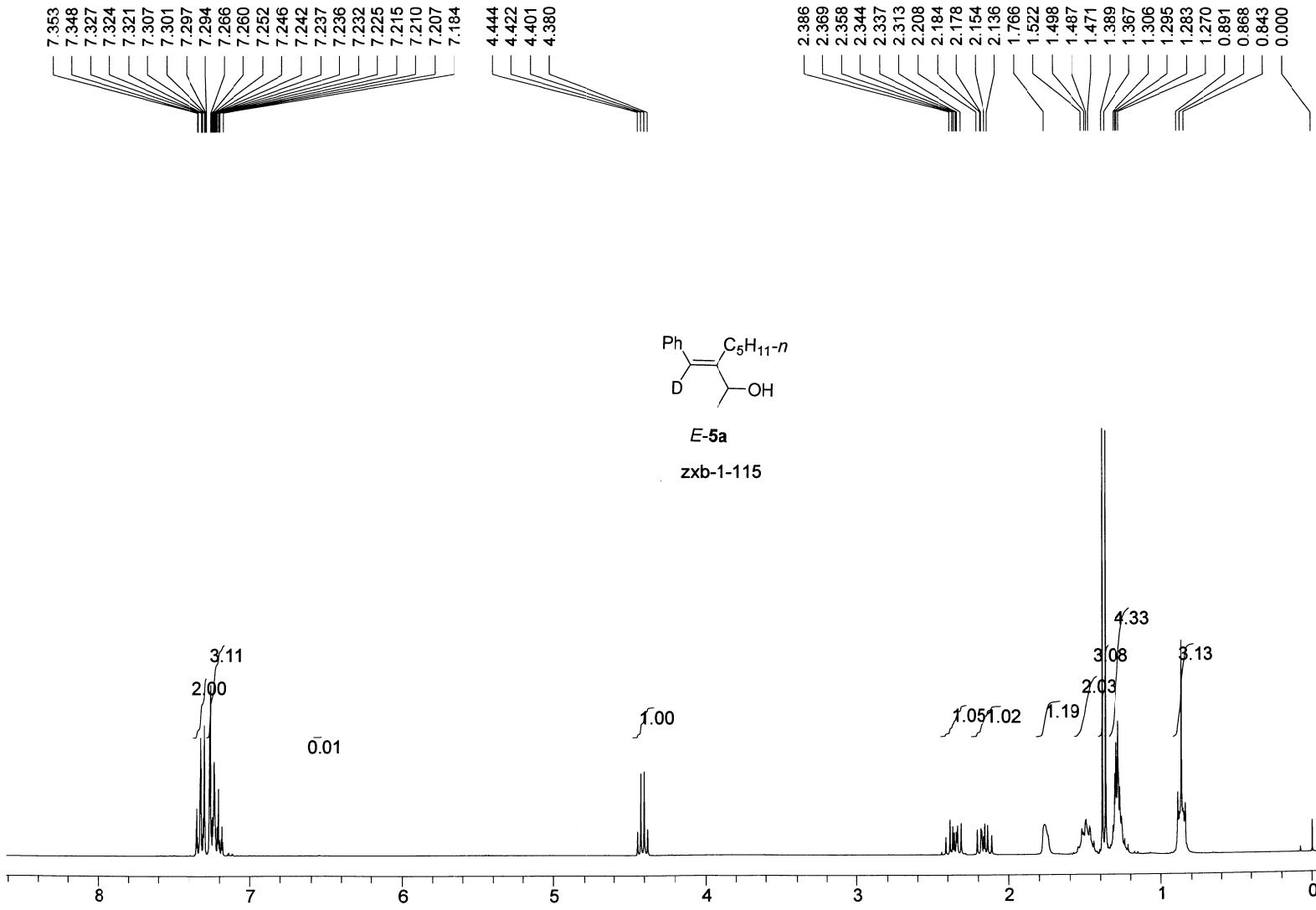
160
140
120
100
80
60
40
20
0 PPM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7.348
7.327
7.324
7.321
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7.266
7.260
7.252
7.246
7.242
7.237
7.236
7.232
7.225
7.215
7.210
7.207
7.184
4.444
4.422
4.401
4.380
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2.369
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2.337
2.313
2.208
2.184
2.178
2.154
2.136
1.766
1.522
1.498
1.487
1.471
1.389
1.367
1.306
1.295
1.283
1.270
0.891
0.868
0.843
0.000
Ph
C5H11-n
D
OH
E-5a
zxb-1-115
3.11
2.00
0.01
1.00
1.05
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3.08
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3.13
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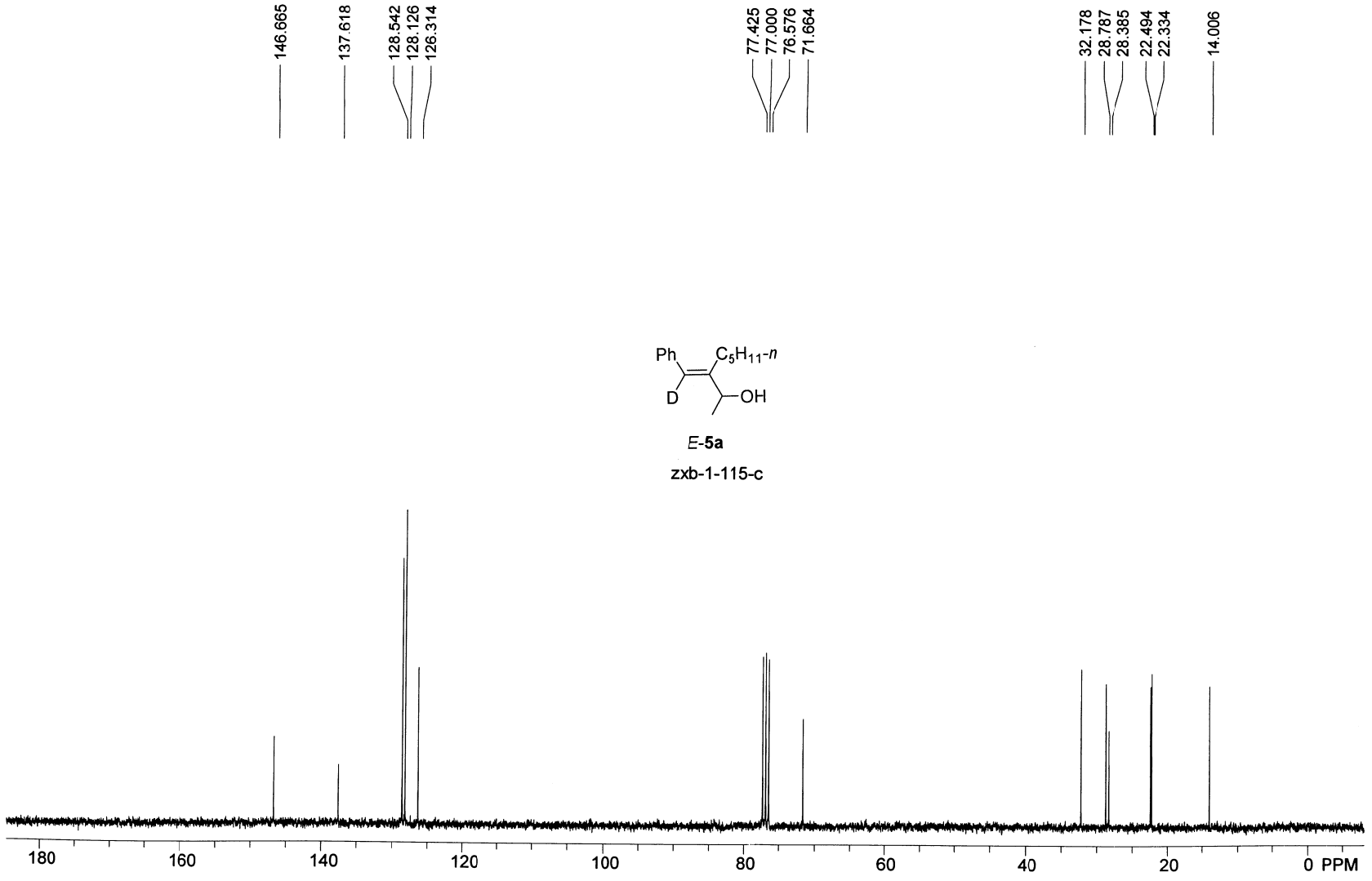
1
0
PPM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126.314
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77.000
76.576
71.664
32.178
28.787
28.385
22.494
22.334
14.006
Ph
C5H11-n
D
OH
E-5a
zxb-1-115-c
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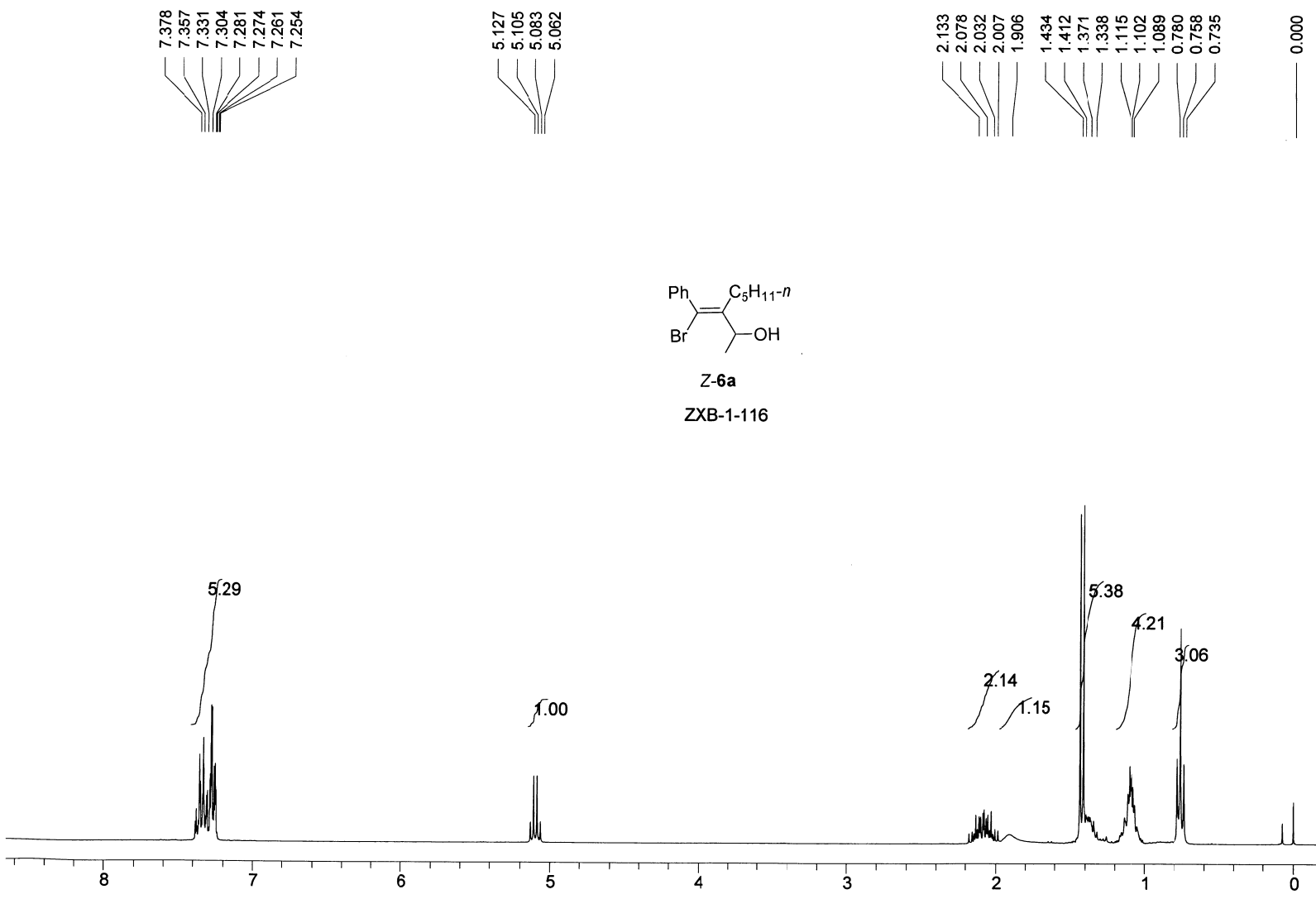
140
120
100
80
60
40
20
0 PPM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7.304
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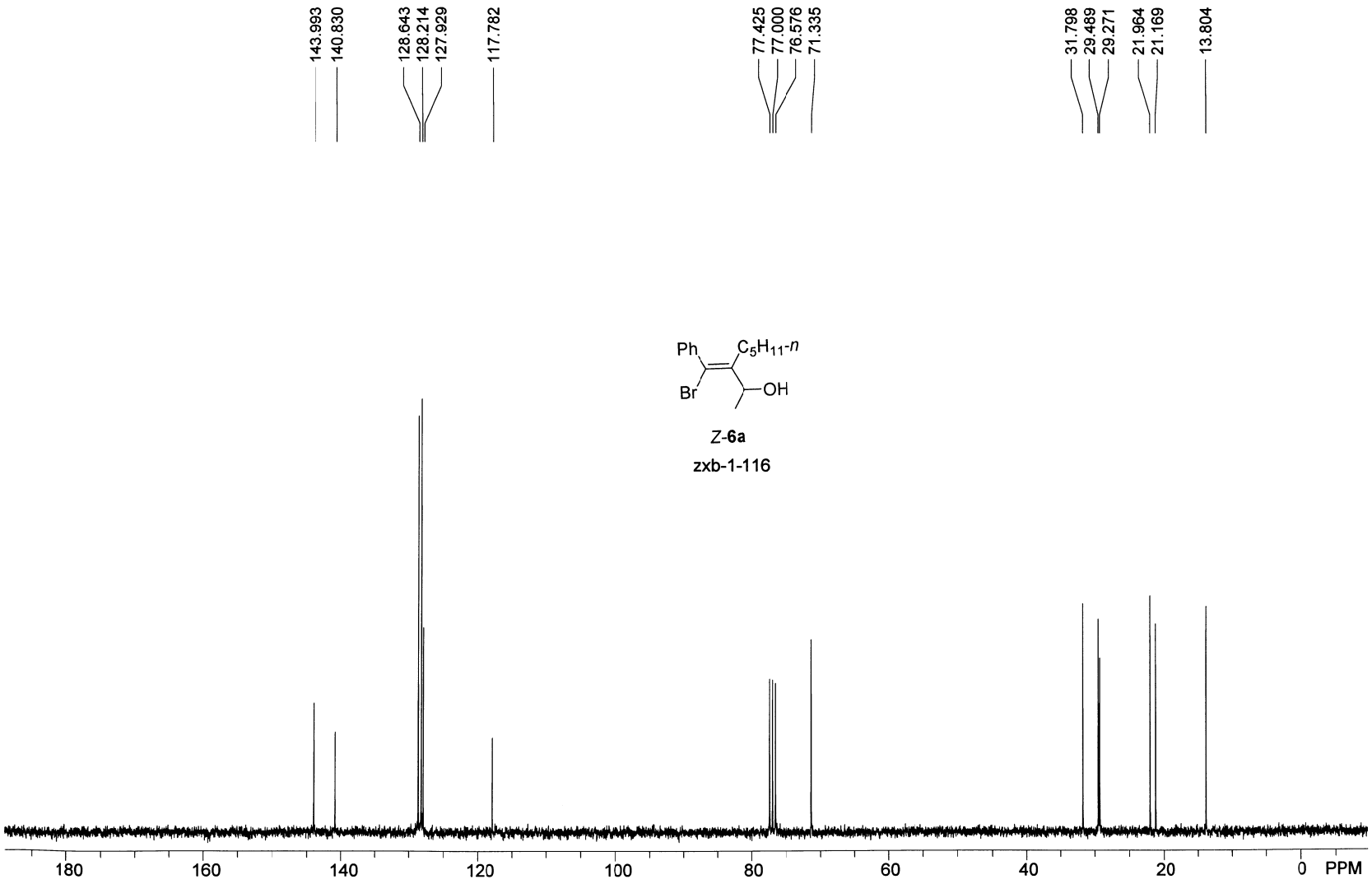
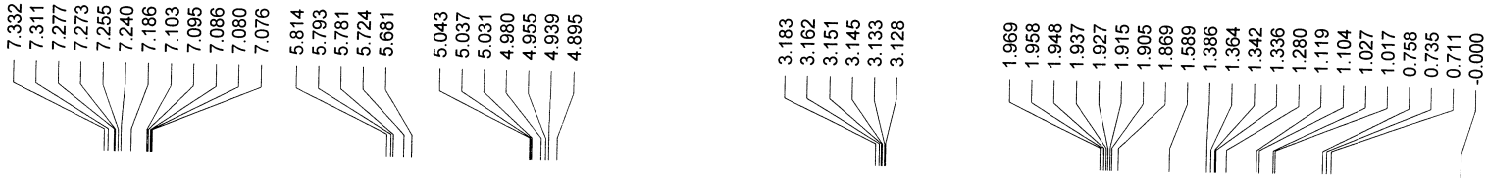
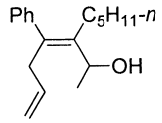
7.274
7.261
7.254
5.127
5.105
5.083
5.062
2.133
2.078
2.032
2.007
1.906
1.434
1.412
1.371
1.338
1.115
1.102
1.089
0.780
0.758
0.735
0.000
Ph
C5H11-n
Br
OH
Z-6a
ZXB-1-116
5.29
1.00
2.14
1.15
5.38
4.21
3.06
8
7
6
5
4
3
2
1
0
PPM

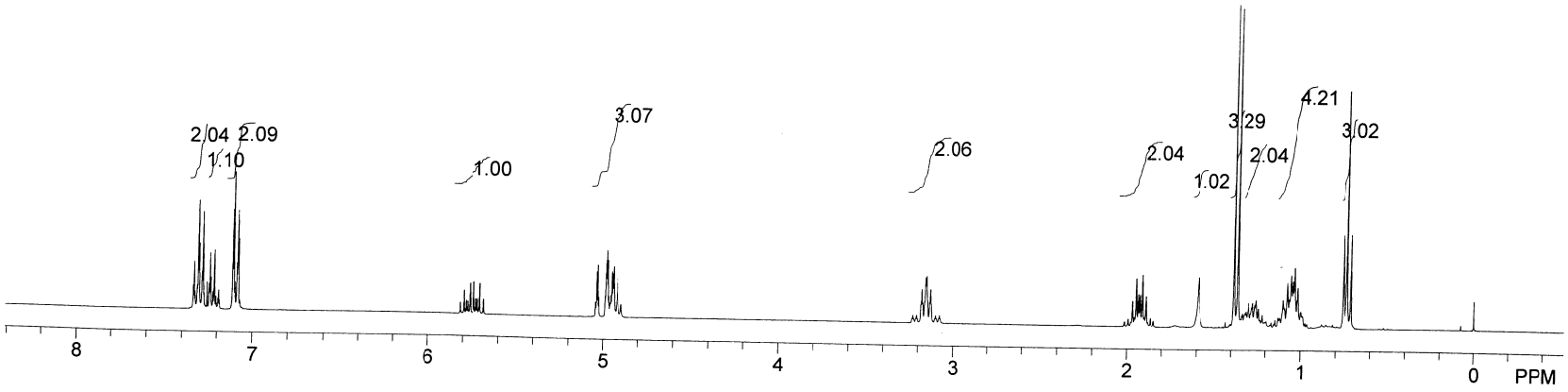

143.993
140.830
128.643
128.214
127.929
117.782
77.425
77.000
76.576
71.335
31.798
29.489
29.271
21.964
21.169
13.804
Ph
C5H11-n
Br
OH
Z-6a
zxb-1-116
180
160
140
120
100
80
60
40
20
0
PPM


7.332
7.311
7.277
7.273
7.255
7.240
7.186
7.103
7.095
7.086
7.080
7.076
5.814
5.793
5.781
5.724
5.681
5.043
5.037
5.031
4.980
4.955
4.939
4.895
3.183
3.162
3.151
3.145
3.133
3.128
1.969
1.958
1.948
1.937
1.927
1.915
1.905
1.869
1.589
1.386
1.364
1.342
1.336
1.280
1.119
1.104
1.027
1.017
0.758
0.735
0.711
-0.000

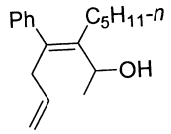

Ph
C5H11-n
OH

E-**7a**

zxb-1-107

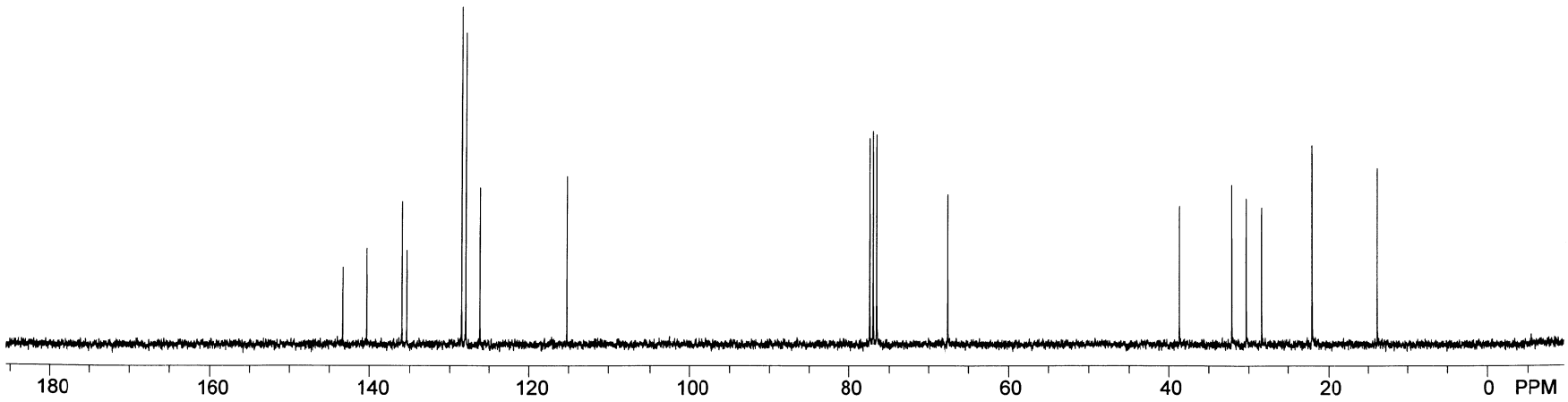

2.04
2.09
1.10
1.00
3.07
2.06
2.04
1.02
3.29
2.04
4.21
3.02
8
7
6
5
4
3
2
1
0
PPM

143.360
140.327
136.048
135.468
128.419
127.905
126.150
115.230
77.422
77.000
76.578
67.552
38.697
32.202
30.307
28.360
22.051
22.038
13.878

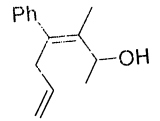


E-**7a**

zxb-1-107-c

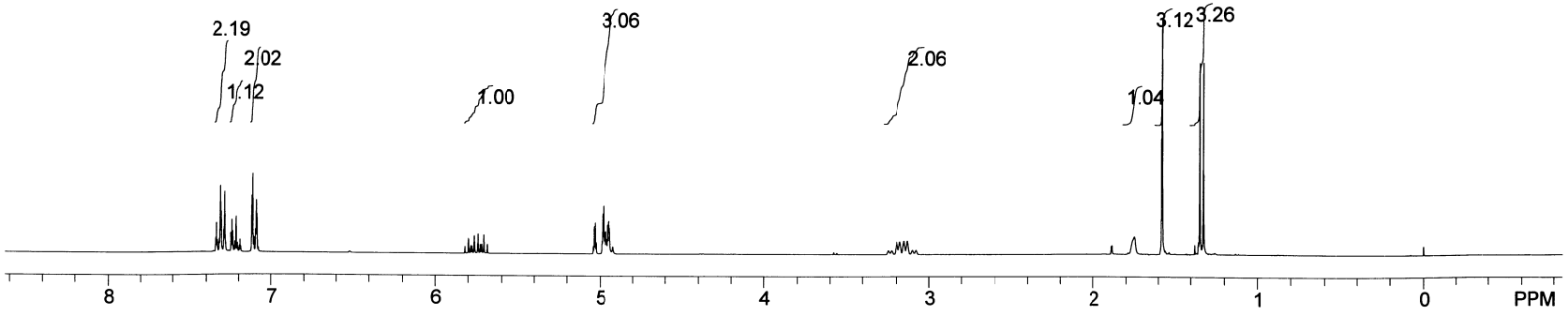


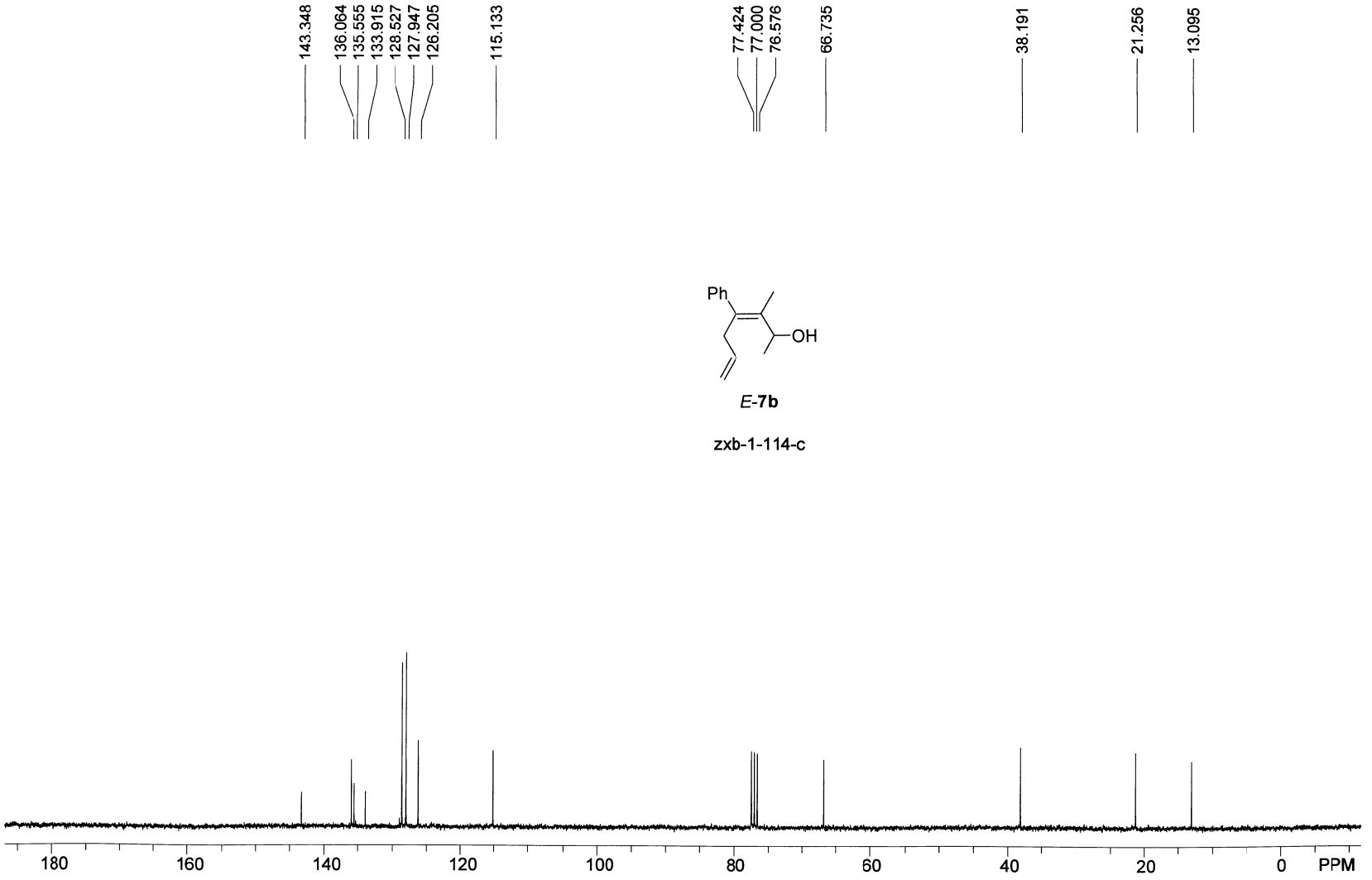

7.334
7.311
7.286
7.241
7.193
7.116
7.090
5.818
5.776
5.764
5.706
5.686
5.037
4.979
4.945
3.175
3.173
3.130
3.127
1.749
1.579
1.346
1.325
0.000


Ph
OH

E-**7b**

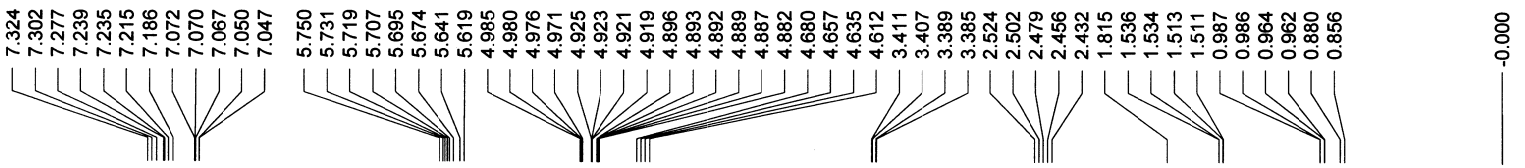
zxb-1-114

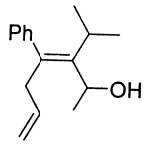

2.19
2.02
1.12
1.00
3.06
2.06
1.04
3.12
3.26
8
7
6
5
4
3
2
1
0
PPM



E-**7b**

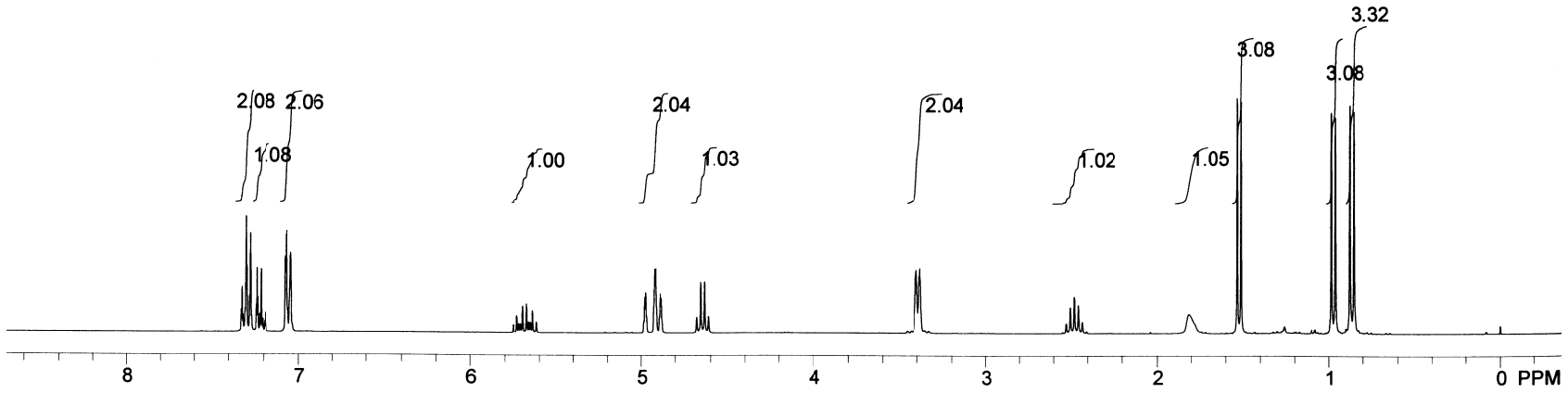
zxb-1-114-c


7.324
7.302
7.277
7.239
7.235
7.215
7.186
7.072
7.070
7.067
7.050
7.047
5.750
5.731
5.719
5.707
5.695
5.674
5.641
5.619
4.985
4.980
4.976
4.971
4.925
4.923
4.921
4.919
4.896
4.893
4.892
4.889
4.887
4.882
4.680
4.657
4.635
4.612
3.411
3.407
3.389
3.385
2.524
2.502
2.479
2.456
2.432
1.815
1.536
1.534
1.513
1.511
0.987
0.986
0.964
0.962
0.880
0.856
-0.000

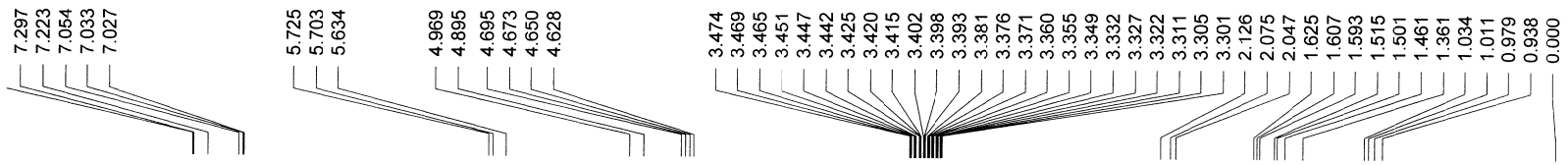

Ph
OH

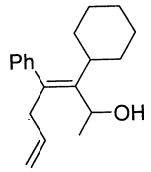
E-**7c**

zxb-2-112


2.08
2.06
1.08
1.00
2.04
1.03
2.04
1.02
1.05
3.08
3.08
3.32
8
7
6
5
4
3
2
1
0 PPM

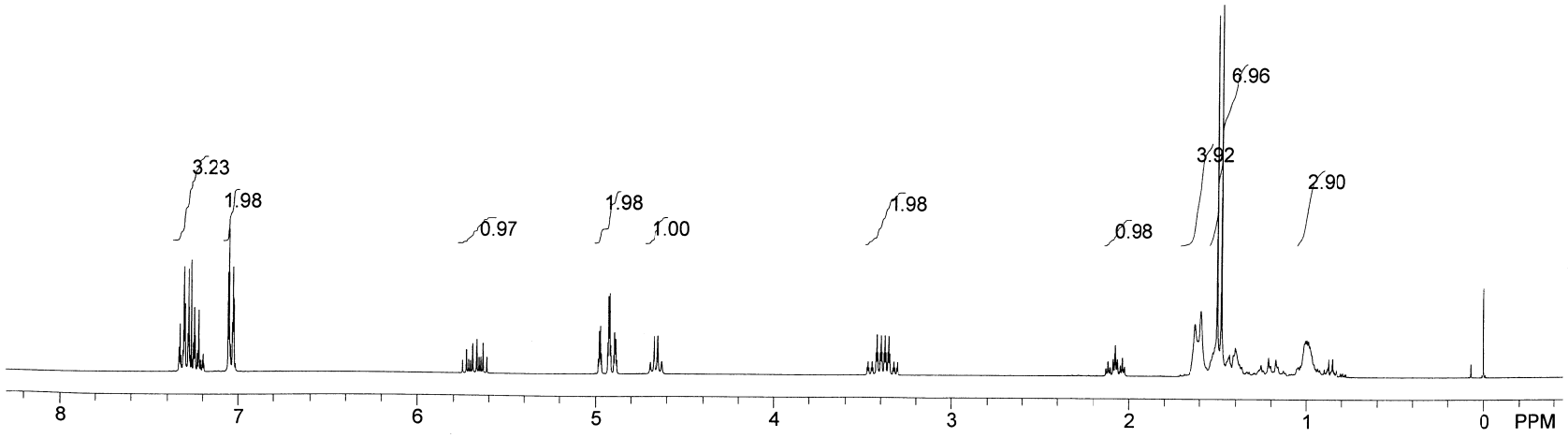
21.243
21.504
23.723
31.110
39.420
65.974
76.574
77.000
77.421
115.424
126.035
127.820
128.427
136.254
136.350
143.227
144.894
OH
Ph
E-7c
zxb-1-112-c
PPM
20
40
60
80
100
120
140
160
180



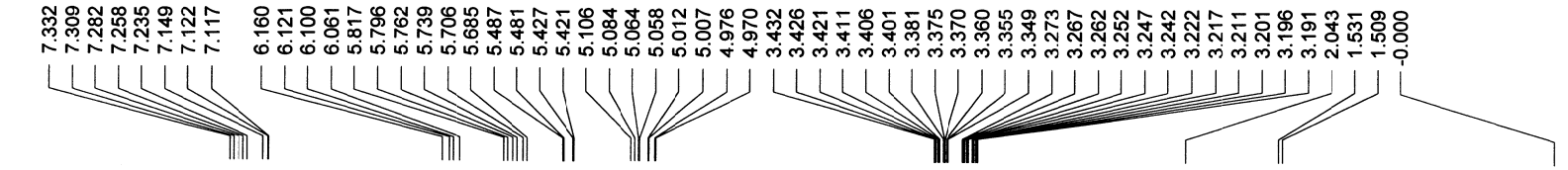


E-**7d**

zxb-2-109-2



23.473
25.907
26.254
26.401
31.355
31.576
39.479
42.260
66.974
76.578
77.000
77.421
115.389
126.092
127.809
128.436
136.411
136.777
143.295
144.842
OH
Ph
E-7d
zxb-1-109-2-c
0PPM
20
40
60
80
100
120
140
160
180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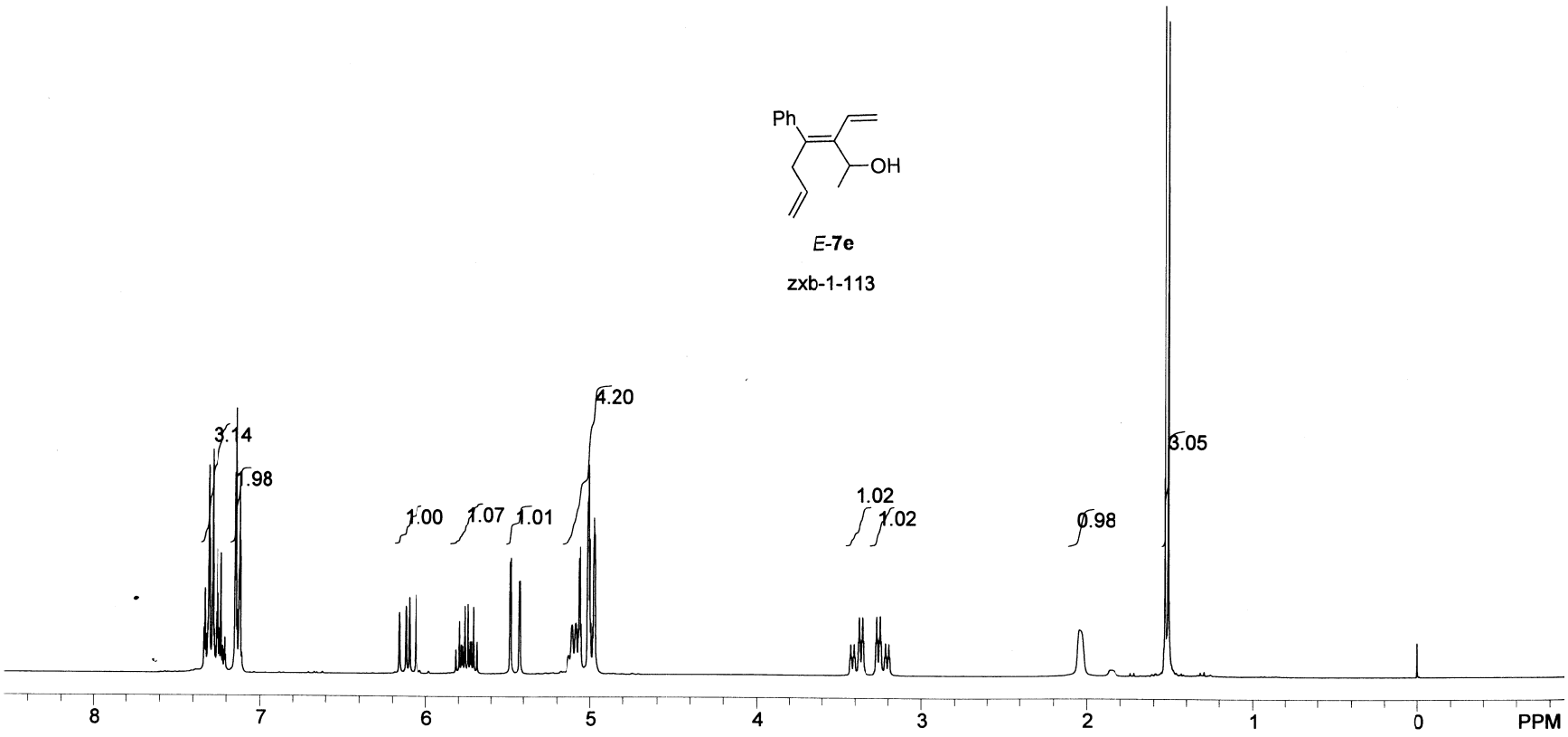
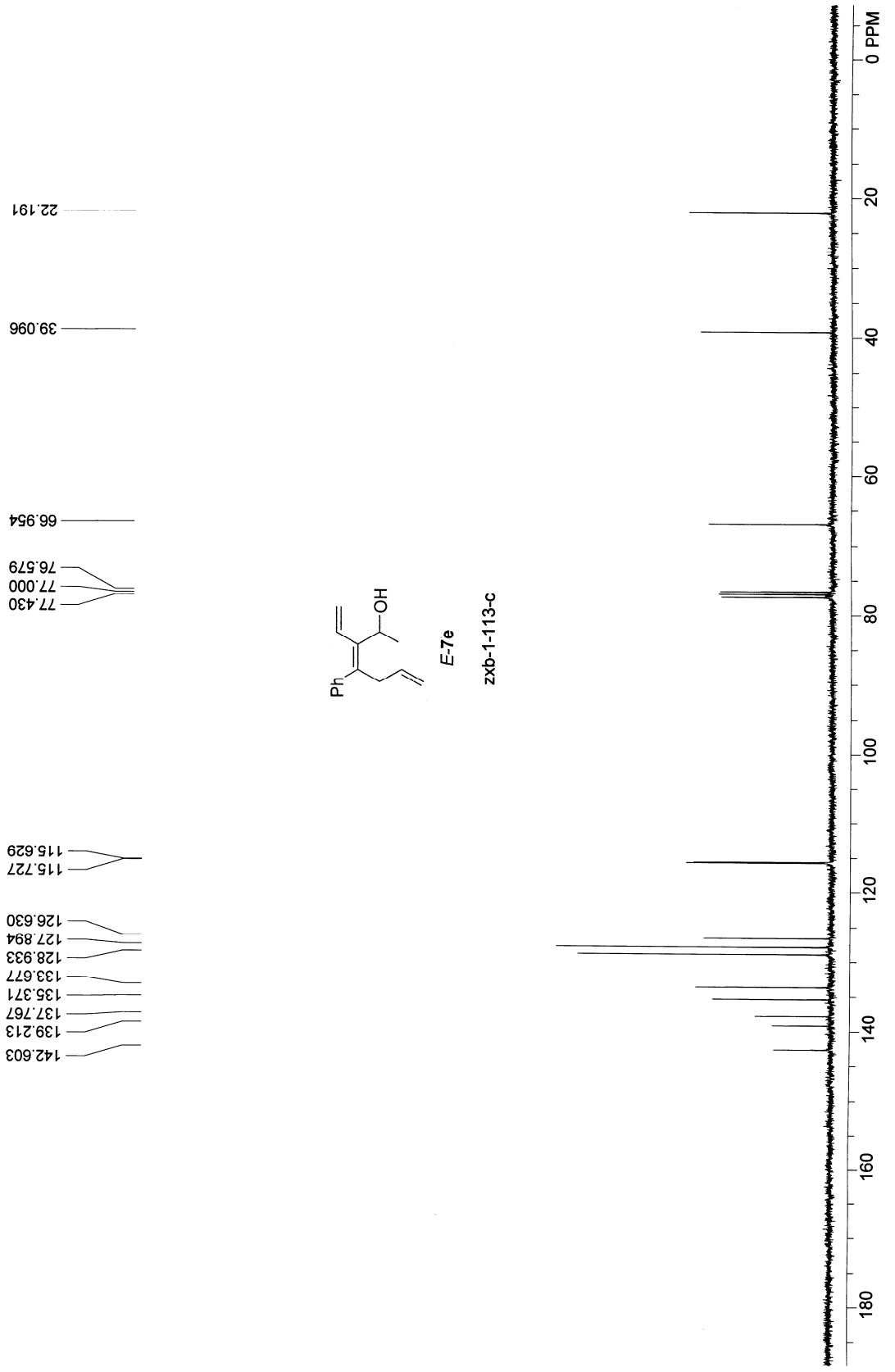
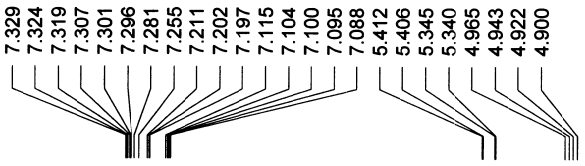
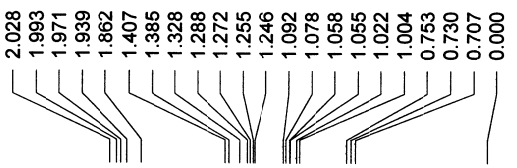
7.309
7.282
7.258
7.235
7.149
7.122
7.117
6.160
6.121
6.100
6.061
5.817
5.796
5.762
5.739
5.706
5.685
5.487
5.481
5.427
5.421
5.106
5.084
5.064
5.058
5.012
5.007
4.976
4.970
3.432
3.426
3.421
3.411
3.406
3.401
3.381
3.375
3.370
3.360
3.355
3.349
3.273
3.267
3.262
3.252
3.247
3.242
3.222
3.217
3.211
3.201
3.196
3.191
2.043
1.531
1.509
-0.000

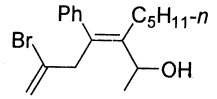

Ph
OH
E-7e
zxb-1-113
3.14
1.98
1.00
1.07
1.01
4.20
1.02
1.02
0.98
3.05
8
7
6
5
4
3
2
1
0
PPM


22.191
39.096
66.954
76.579
77.000
77.430
115.629
115.727
126.630
127.894
128.933
133.677
135.371
137.767
139.213
142.603
Ph
OH
E-7e
zxb-1-113-c
0 PPM
20
40
60
80
100
120
140
160
180


7.329
7.324
7.319
7.307
7.301
7.296
7.281
7.255
7.211
7.202
7.197
7.115
7.104
7.100
7.095
7.088
5.412
5.406
5.345
5.340
4.965
4.943
4.922
4.900

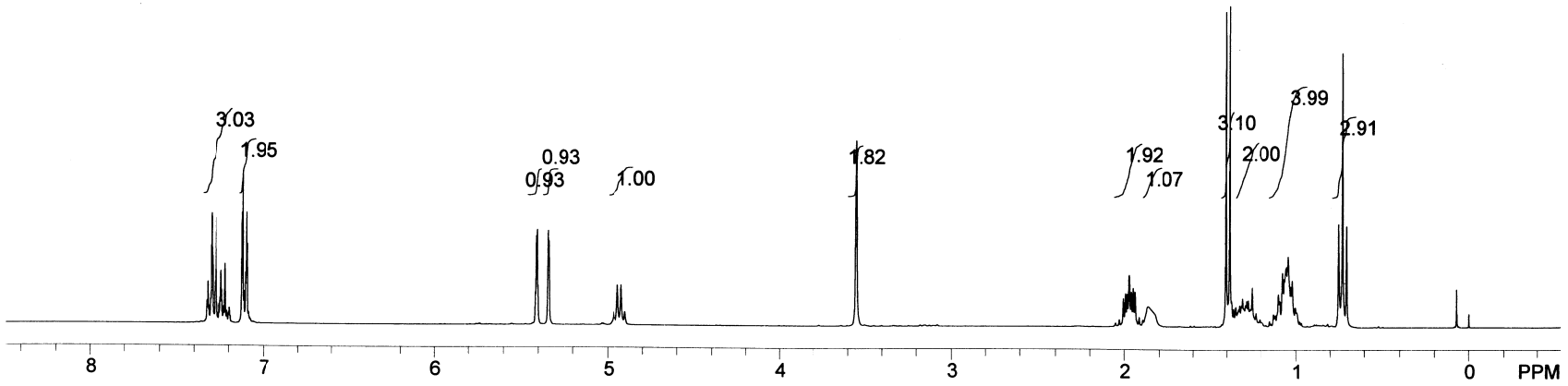
3.552

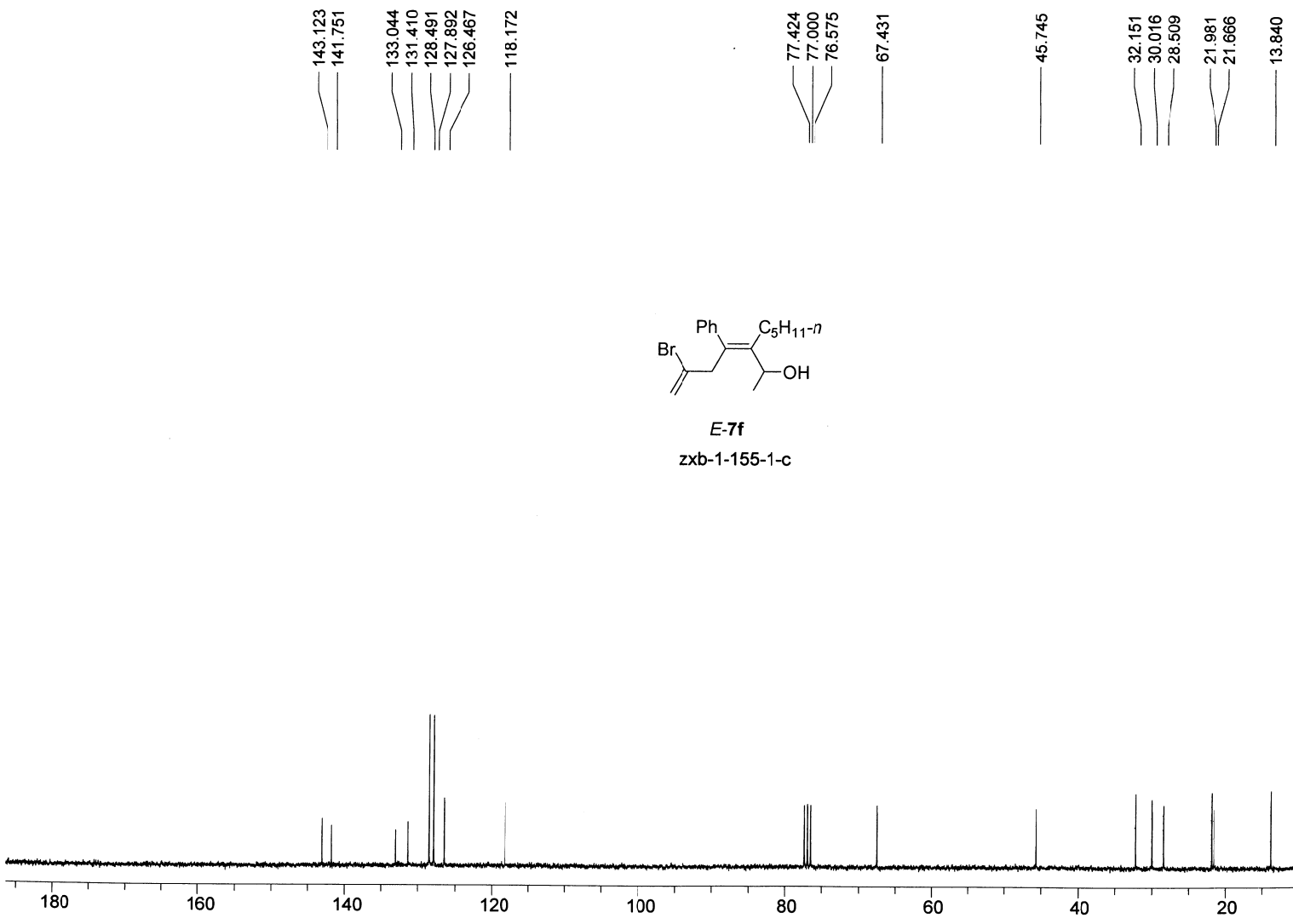

2.028
1.993
1.971
1.939
1.862
1.407
1.385
1.328
1.288
1.272
1.255
1.246
1.092
1.078
1.058
1.055
1.022
1.004
0.753
0.730
0.707
0.000

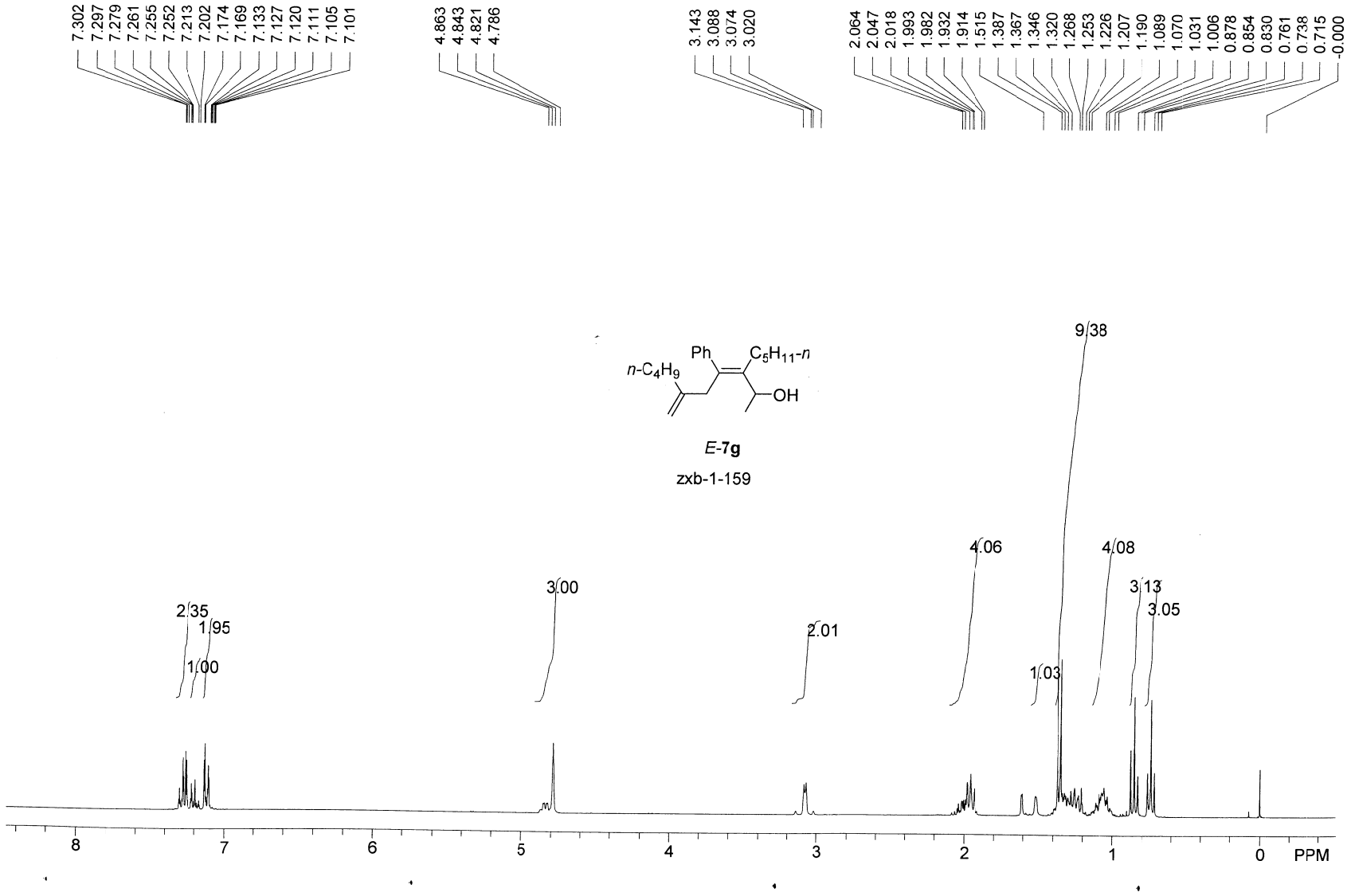

Ph
C_5H_{11}-*n*
Br
OH

***E*-7f**

zxb-1-155


3.03
1.95
0.93
0.93
1.00
1.82
1.92
1.07
3.10
2.00
3.99
2.91
8
7
6
5
4
3
2
1
0
PPM


143.123
141.751
133.044
131.410
128.491
127.892
126.467
118.172
77.424
77.000
76.575
67.431
45.745
32.151
30.016
28.509
21.981
21.666
13.840
Ph
C5H11-n
Br
OH
E-7f
zxb-1-155-1-c
180
160
140
120
100
80
60
40
20
0PPM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7.261
7.255
7.252
7.213
7.202
7.174
7.169
7.133
7.127
7.120
7.111
7.105
7.101
4.863
4.843
4.821
4.786
3.143
3.088
3.074
3.020
2.064
2.047
2.018
1.993
1.982
1.932
1.914
1.515
1.387
1.367
1.346
1.320
1.268
1.253
1.226
1.207
1.190
1.089
1.070
1.031
1.006
0.878
0.854
0.830
0.761
0.738
0.715
-0.000
Ph
C5H11-n
n-C4H9
OH
E-7g
zxb-1-159
9.38
4.06
4.08
3.13
3.05
3.00
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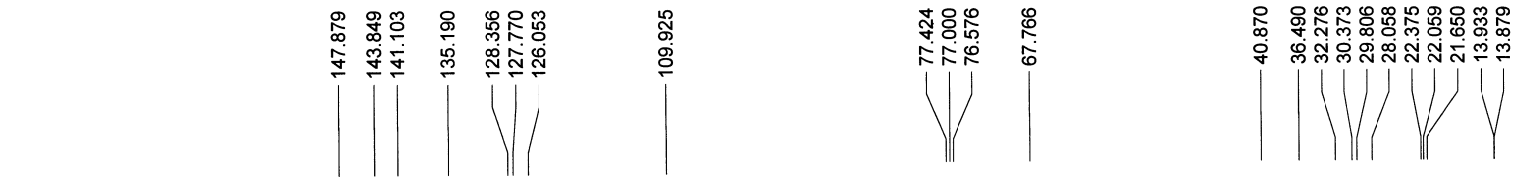
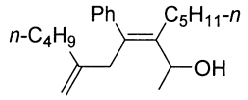
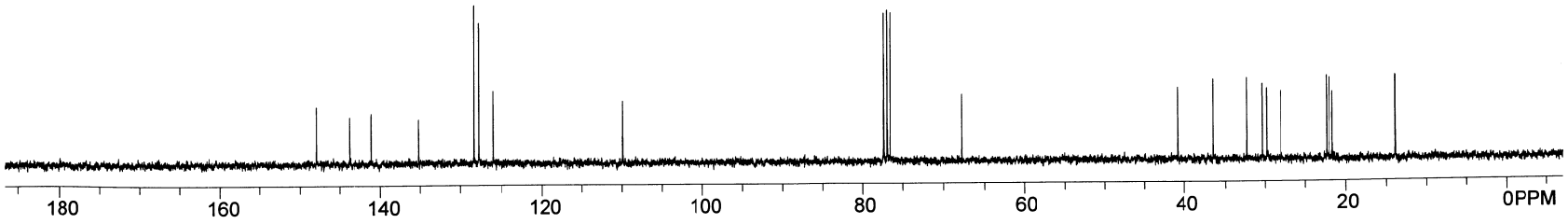
1.00
2.01
1.03
8
7
6
5
4
3
2
1
0
PPM

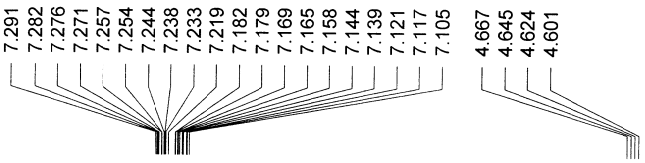




E-**7g**

ZXB-1-159-C

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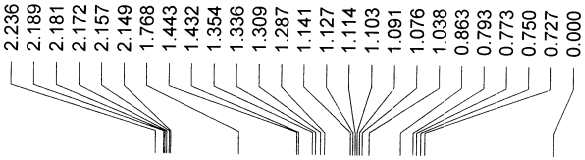
7.271
7.257
7.254
7.244
7.238
7.233
7.219
7.182
7.179
7.169
7.165
7.158
7.144
7.139
7.121
7.117
7.105
4.667
4.645
4.624
4.601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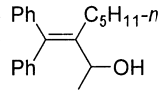
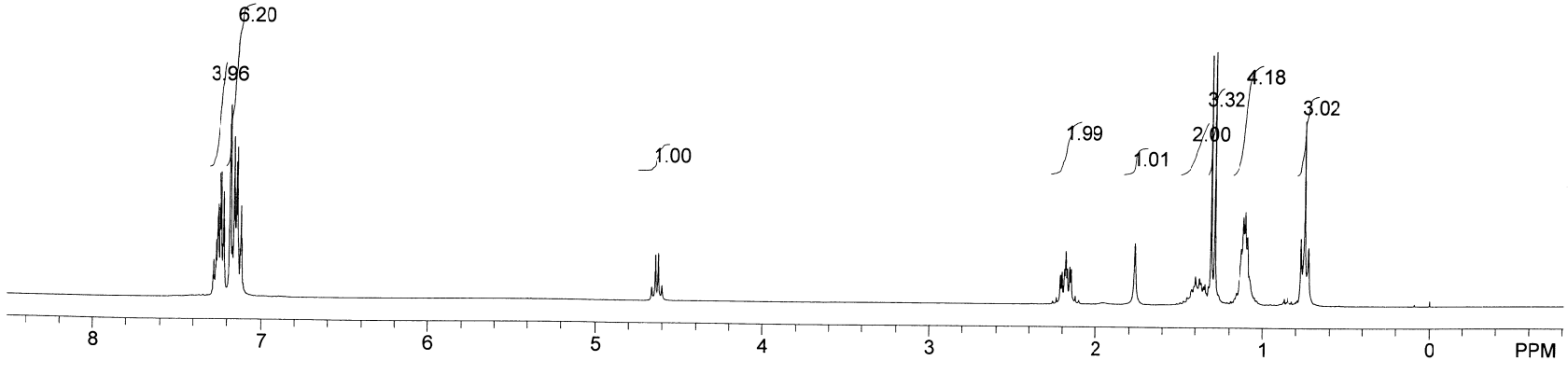
2.189
2.181
2.172
2.157
2.149
1.768
1.443
1.432
1.354
1.336
1.309
1.287
1.141
1.127
1.114
1.103
1.091
1.076
1.038
0.863
0.793
0.773
0.750
0.727
0.000


Ph
C5H11-n
Ph
OH

8a

zxb-1-117-1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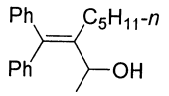
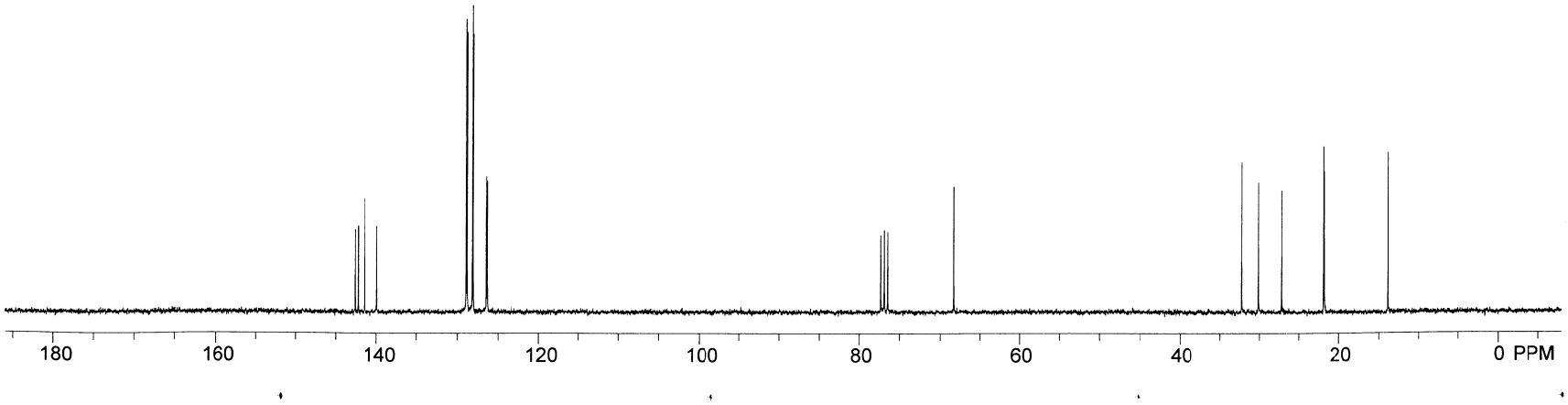
1.00
1.99
1.01
2.00
3.32
4.18
3.02
8
7
6
5
4
3
2
1
0
PPM

142.609
142.240
141.466
139.931
128.832
128.713
128.074
128.005
126.412
126.286
77.421
77.000
76.580
68.256
32.225
30.168
27.285
22.014
21.915
13.848



8a

zxb-1-117-1-c




7.307
7.273
7.255
7.249
7.244
7.205
7.165
7.161
7.139
6.994
6.992
6.959
6.957
6.953
6.950
6.947
6.940
4.669
4.647
4.625
4.604
2.294
2.221
2.198
2.186
2.174
2.165
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2.141
2.132
2.108
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1.459
1.430
1.392
1.378
1.325
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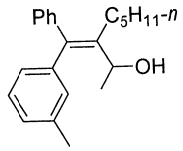
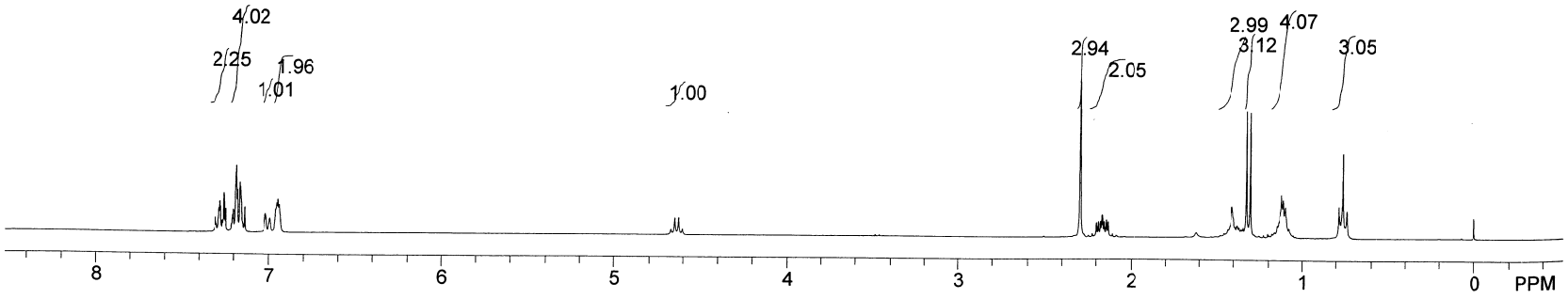
1.133
1.122
1.078
1.063
0.784
0.761
0.738
0.000


Ph
C5H11-n
OH

Z-**8b**

zxb-2-52-1


4.02
2.25
1.96
1.01
1.00
2.94
2.05
2.99
3.12
4.07
3.05
8
7
6
5
4
3
2
1
0
PPM

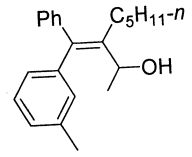
142.719
142.272
141.319
140.269
137.733
129.448
128.706
128.068
128.024
127.283
126.316
125.900

77.425
77.000
76.576

68.483

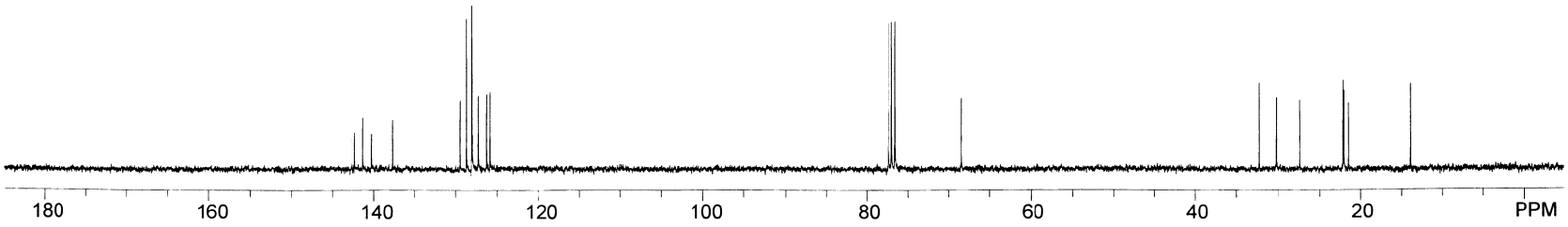
32.308
30.275
27.393
22.093
21.984
21.435

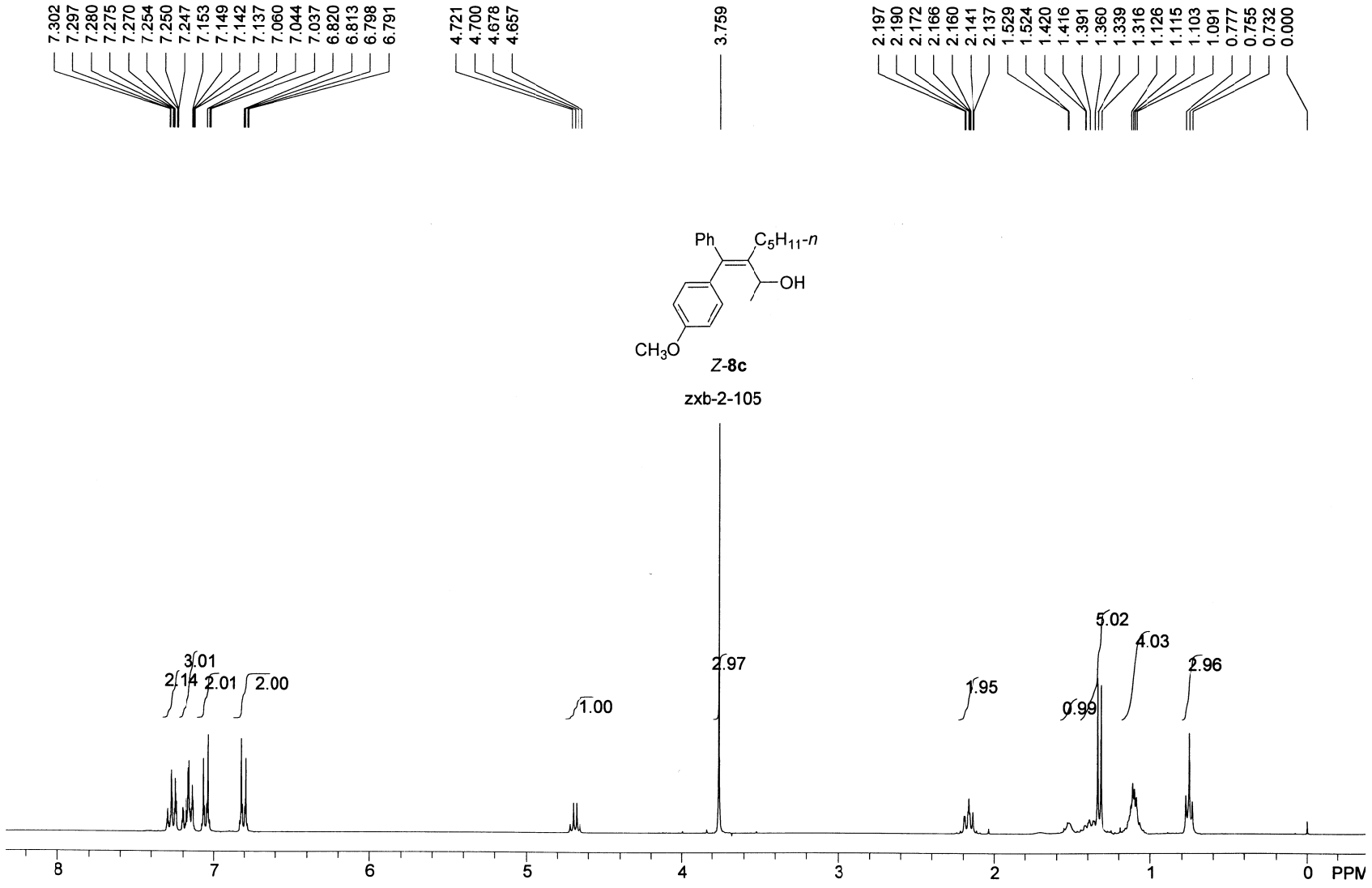
13.892



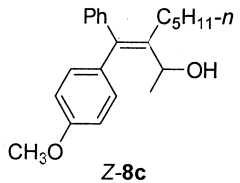
Z-**8b**

zxb-2-54-1-c



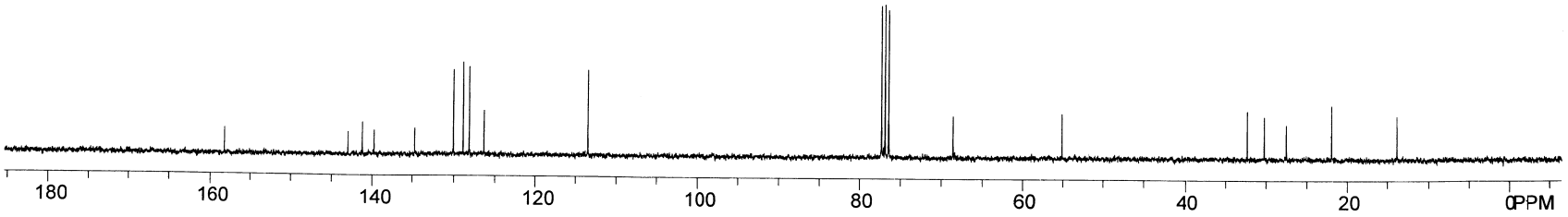

7.302
7.297
7.280
7.275
7.270
7.254
7.250
7.247
7.153
7.149
7.142
7.137
7.060
7.044
7.037
6.820
6.813
6.798
6.791
4.721
4.700
4.678
4.657
3.759
2.197
2.190
2.172
2.166
2.160
2.141
2.137
1.529
1.524
1.420
1.416
1.391
1.360
1.339
1.316
1.126
1.115
1.103
1.091
0.777
0.755
0.732
0.000
Ph
C5H11-n
OH
CH3O
Z-8c
zxb-2-105
3.01
2.14
2.01
2.00
1.00
2.97
1.95
0.99
5.02
4.03
2.96
8
7
6
5
4
3
2
1
0
PPM

158.184
143.034
141.216
139.778
134.709
130.061
128.788
128.057
126.288
113.513
77.424
77.000
76.576
68.496
55.165
32.297
30.277
27.513
22.094
22.038
13.895

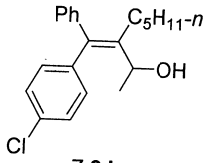


Z-**8c**

zxb-2-43-3-1-c

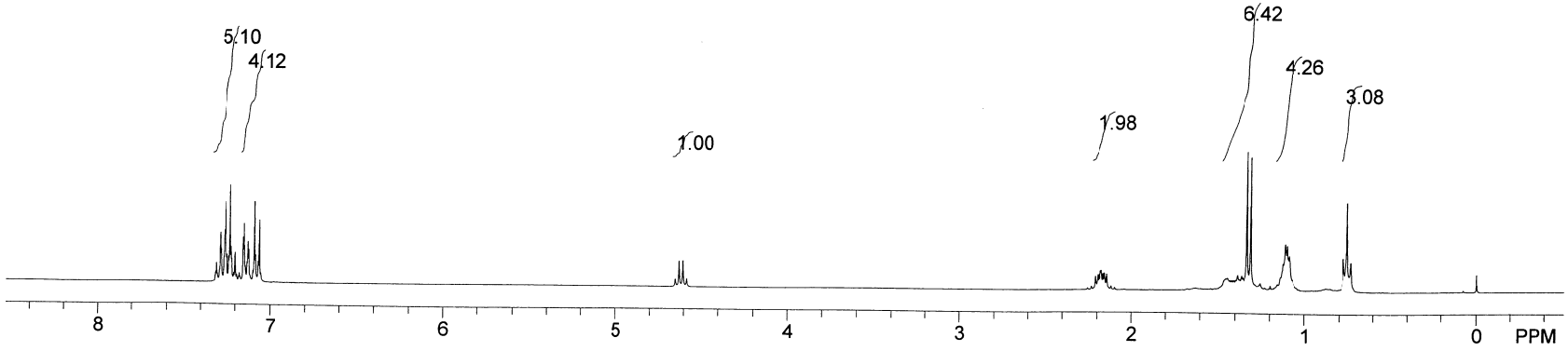


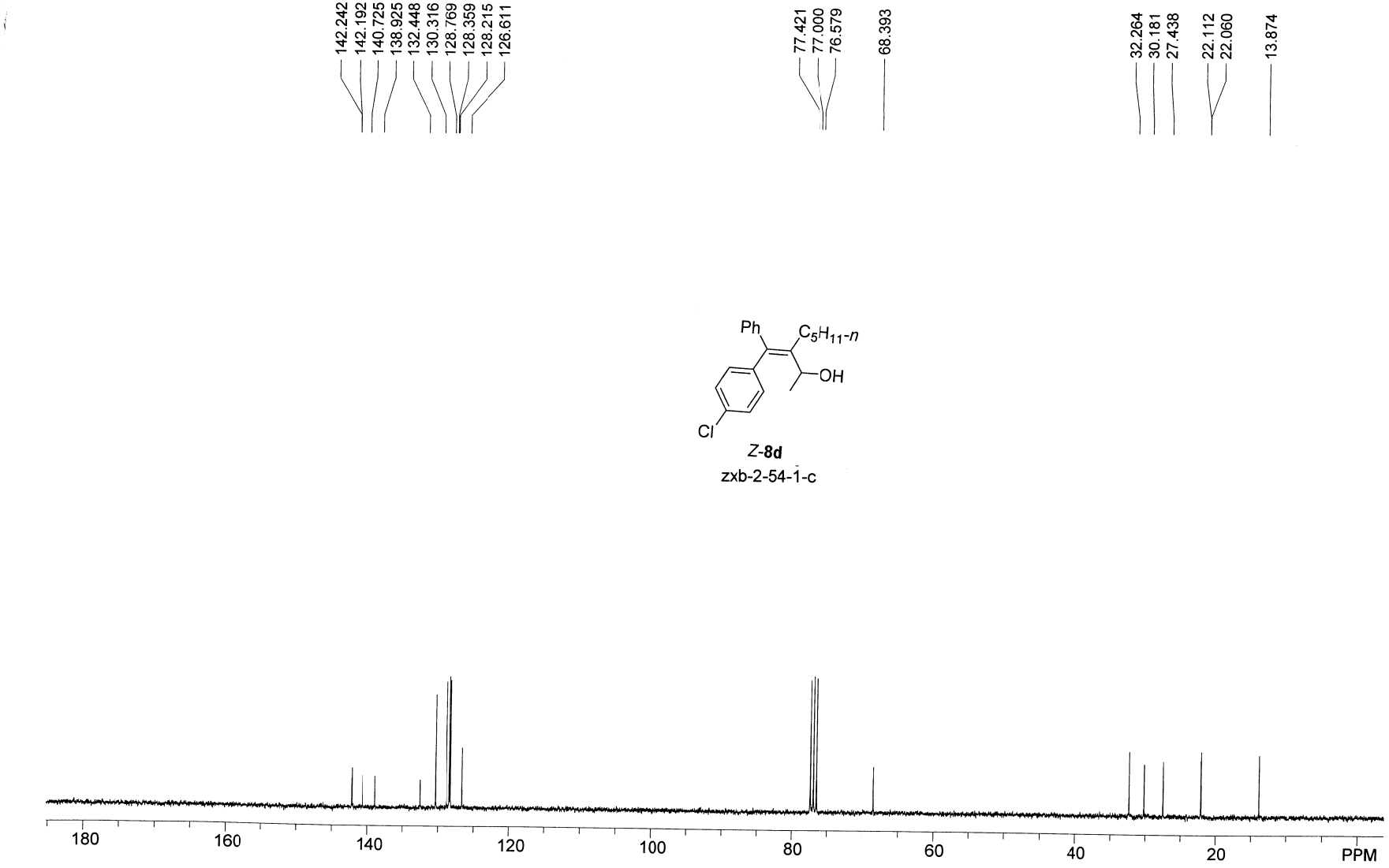

7.312
7.294
7.288
7.264
7.259
7.252
7.230
7.200
7.192
7.132
7.123
7.091
7.084
4.647
4.626
4.604
4.583
2.195
2.178
2.154
1.445
1.431
1.420
1.331
1.309
1.158
1.141
1.126
1.114
1.091
1.073
0.777
0.755
0.731
-0.000
-0.002

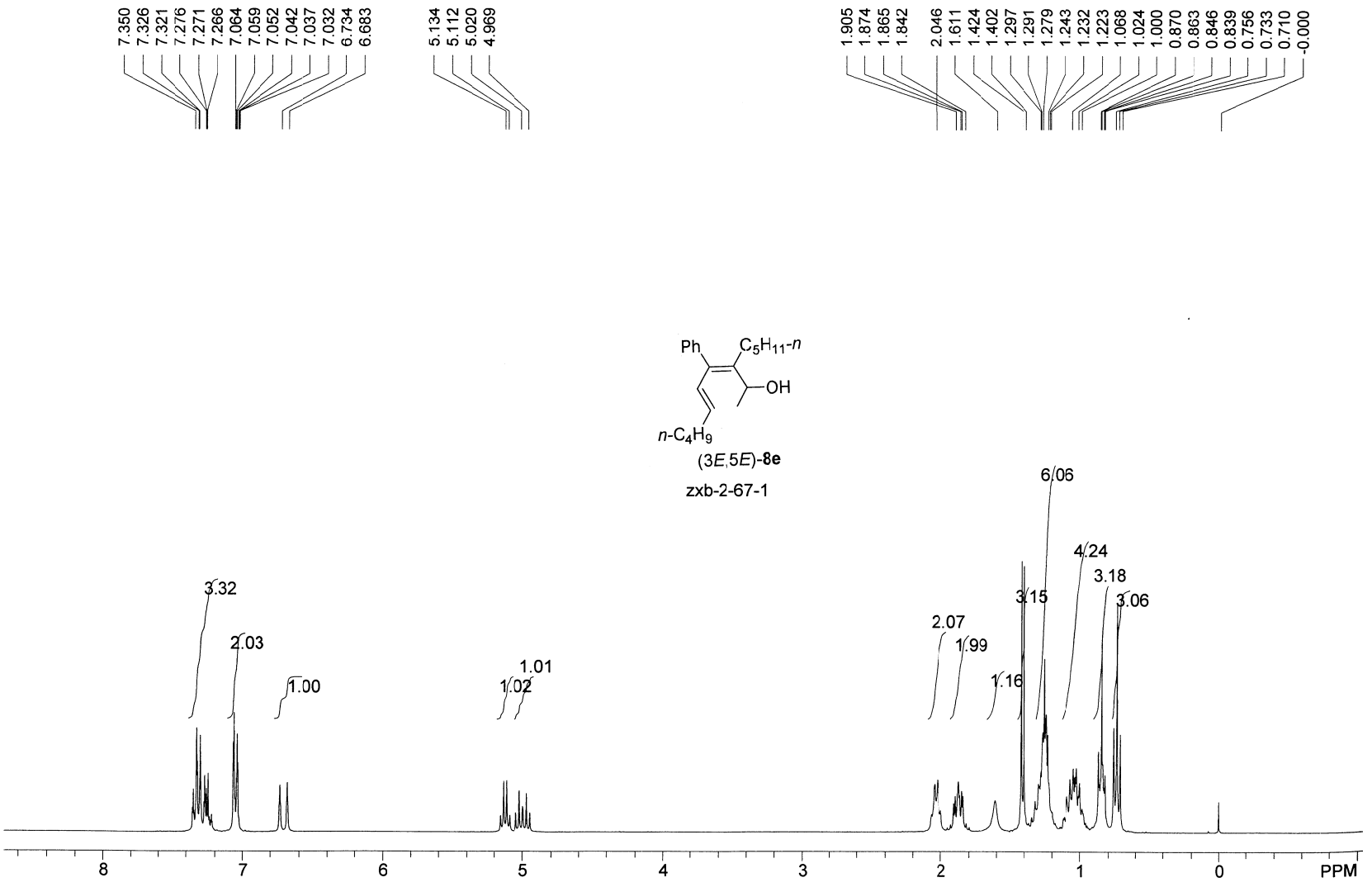

Ph
C_5H_{11}-*n*
OH
Cl

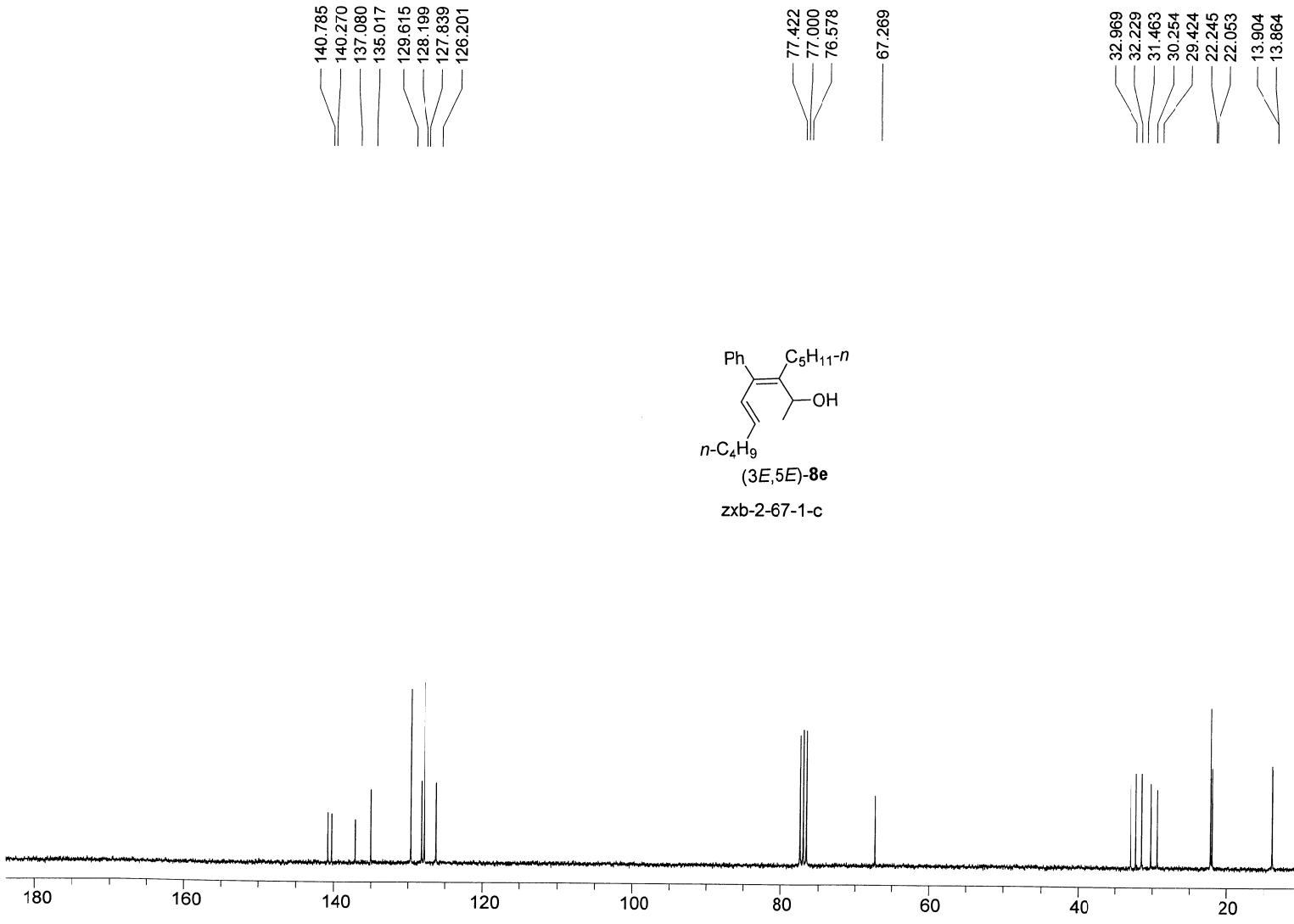
Z-**8d**

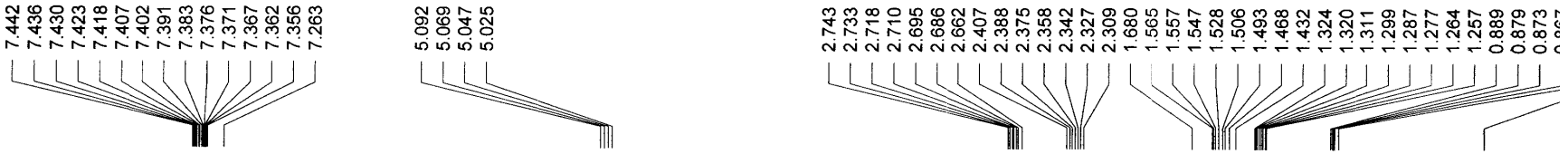
zxb-2-54-1

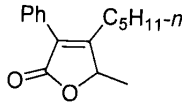

5.10
4.12
1.00
1.98
6.42
4.26
3.08
8
7
6
5
4
3
2
1
0
PPM


142.242
142.192
140.725
138.925
132.448
130.316
128.769
128.359
128.215
126.611
77.421
77.000
76.579
68.393
32.264
30.181
27.438
22.112
22.060
13.874
Ph
C5H11-n
OH
Cl
Z-8d
zxb-2-54-1-c
180
160
140
120
100
80
60
40
20
PPM


7.350
7.326
7.321
7.276
7.271
7.266
7.064
7.059
7.052
7.042
7.037
7.032
6.734
6.683
5.134
5.112
5.020
4.969
1.905
1.874
1.865
1.842
2.046
1.611
1.424
1.402
1.297
1.291
1.279
1.243
1.232
1.223
1.068
1.024
1.000
0.870
0.863
0.846
0.839
0.756
0.733
0.710
-0.000
Ph
C5H11-n
OH
n-C4H9
(3E,5E)-8e
zxb-2-67-1
3.32
2.03
1.00
1.02
1.01
2.07
1.99
1.16
3.15
6.06
4.24
3.18
3.06
8
7
6
5
4
3
2
1
0
PPM

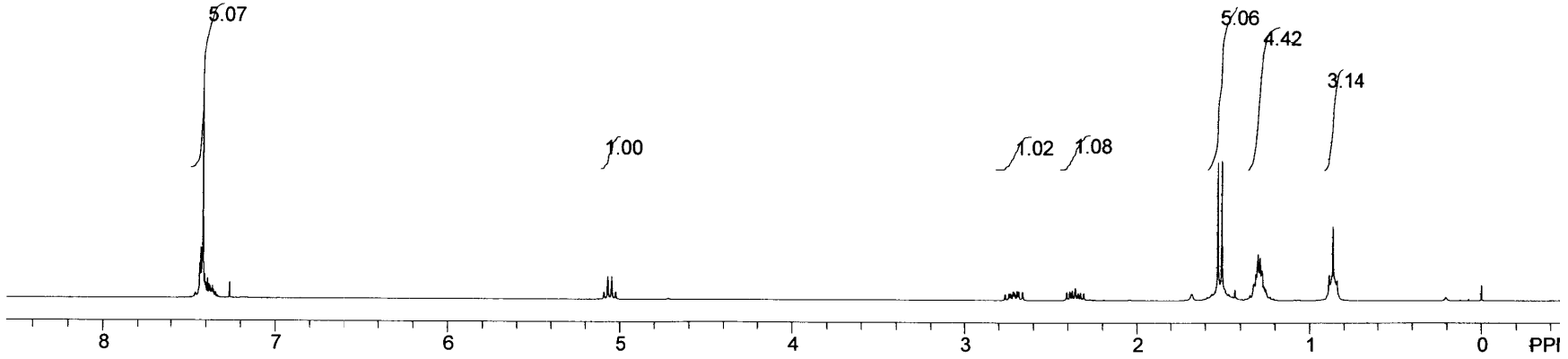

140.785
140.270
137.080
135.017
129.615
128.199
127.839
126.201
77.422
77.000
76.578
67.269
32.969
32.229
31.463
30.254
29.424
22.245
22.053
13.904
13.864
Ph
C_5H_{11}-*n*
OH
n-C_4H_9
(3*E*,5*E*)-**8e**
zxb-2-67-1-c
180
160
140
120
100
80
60
40
20
0PPM


7.442
7.436
7.430
7.423
7.418
7.407
7.402
7.391
7.383
7.376
7.371
7.367
7.362
7.356
7.263
5.092
5.069
5.047
5.025
2.743
2.733
2.718
2.710
2.695
2.686
2.662
2.407
2.388
2.375
2.358
2.342
2.327
2.309
1.680
1.565
1.557
1.547
1.528
1.506
1.493
1.468
1.432
1.324
1.320
1.311
1.299
1.287
1.277
1.264
1.257
0.889
0.879
0.873


Ph
C5H11-n
O
O

9a

zxb-1-138-2


5.07
1.00
1.02
1.08
5.06
4.42
3.14
8
7
6
5
4
3
2
1
0
PPI

13.752
18.272
22.110
26.713
27.355
31.594
76.576
77.000
77.424
77.903
126.392
128.249
128.341
128.821
130.029
166.082
172.559
Ph
C_5H_{11}-n
O
O
9a
zxb-1-138-2-c
PPM
20
40
60
80
100
120
140
160
180