Supporting Information

Diastereoselective Construction of Cyclopent-2-enone-4-ols from Aldehydes and 1,2-Allenones Catalyzed by *N*-Heterocyclic Carbene

Dengke Ma, Chunling Fu, and Shengming Ma*

Laboratory of Molecular Recognition and Synthesis, Department of Chemistry, Zhejiang University, Hangzhou 310027, Zhejiang, People's Republic of China

Fax: (+86) 21-55665687

E-mail: masm@sioc.ac.cn

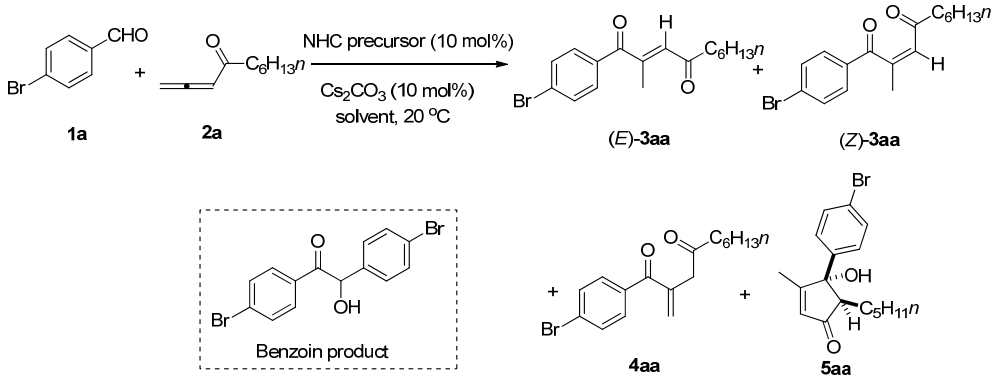
General: ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AM 300 MHz spectrometer. IR spectra were recorded with a Perkin–Elmer 983G instrument. Elemental analyses were measured with a Carlo-Erba EA1110 elementary analysis instrument. Mass spectrometry was performed with an HP 5989A system. High-resolution mass spectrometry was determined with a Finnigan MAT 8430 or Bruker APEXIII instrument. 1-Ethyl-3-methylimidazolium tetrafluoroborate was purchased from J&K. Cs_2CO_3 was purchased from Energy Chemical. 1,4-Dioxane and toluene were distilled from Na/benzophenone before use. CH_2Cl_2 was distilled from CaH_2 before use. All liquid aldehydes were freshly distilled before use. Unless otherwise indicated, chemicals and solvents were purchased from commercial suppliers.

1,2-Allenones **2a**,[1] **2b**,[2] **2c**,[3] **2e**[4], and **2f**[3,5] were prepared according to reported literatures.

Experimental details and analytical data

1. Optimization of the reaction conditions.

Table S1 Reaction exploration[a]



Entry	X	NHC precursor	solvent	t (h)	Product yield[b]%				Recovery of **2a**[b]%
					(*E*)-**3aa**	(*Z*)-**3aa**	**4aa**	**5aa**	
1	2	**A1**	toluene	22.5	37	4	3	—	2
2	2	**A2**	toluene	22.5	38	3	5	—	—
3	2	**B1**	toluene	27.5	4	—	—	—	12
4	2	**B2**	toluene	27.5	—	—	—	—	55
5	2	**B3**	toluene	8.5	18	2	3	—	—
6	2	**C**	toluene	23.5	—	—	1	—	78
7[c]	2	**D**	toluene	23.5	—	—	—	—	64
8[d]	2	**E**	toluene	23.5	—	—	4	—	78
9	1.2	**A1**	toluene	22.5	34	4	2	3[e]	24
10	1.2	**A1**	dioxane	3	24	4	5	40[f]	—
11	1.2	**A1**	THF	27.5	29	2	3	9[g]	5
12	1.2	**A1**	DCM	15.5	49	6	10	12[h]	—
13[i]	1.2	**A1**	DMF	21.8	—	—	—	—	—
14[i]	1.2	**A1**	CH_3CN	22	4	—	—	—	—
15	1.2	**A1**	CH_3OH	24	—	—	—	—	—

[a] Reaction conditions: A solution of NHC precursor and Cs_2CO_3 in solvent (1 mL) was stirred at 20 °C for 10 min, then 0.8 mmol of **1a**, 0.4 mmol of **2a**, and solvent (1 mL) were added sequentially. The resulting mixture was then stirred at 20 °C for the time indicated in the Table. [b] Determined by NMR of the crude product using dibromomethane as the internal standard. [c] The Benzoin product was formed in 39% yield. [d] The Benzoin product was formed in 74% yield. [e] Dr was 100:0 as determined by NMR. [f] Dr was 95:5 as determined by NMR. [g] Dr was 88:12 as determined by NMR. [h] Dr was 100:0 as determined by NMR. [i] 20 mol % of Cs_2CO_3 was used.

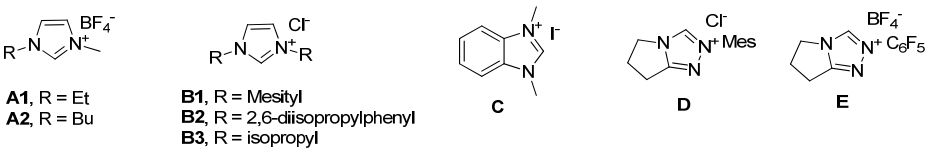
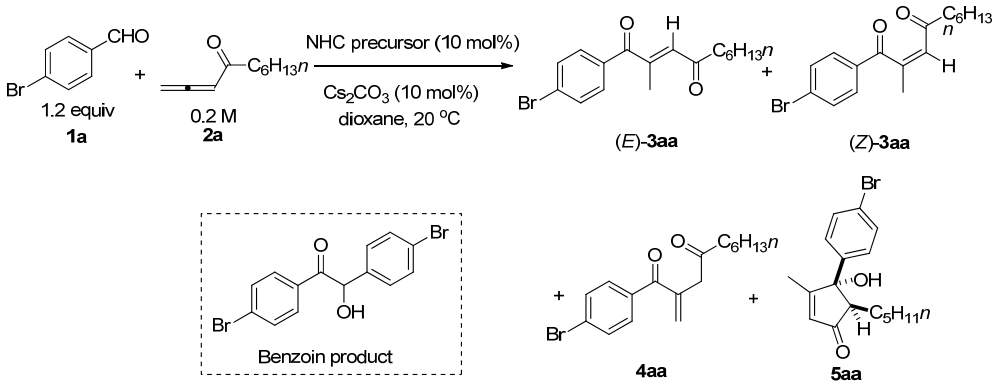
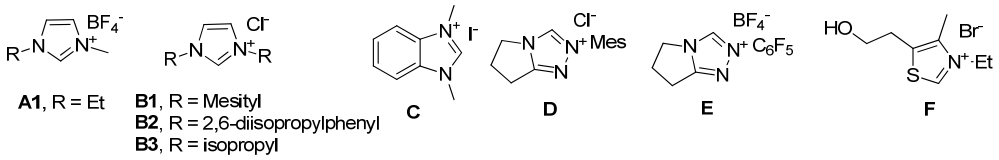


Table S2 Exploration of the NHCs in dioxane[a]



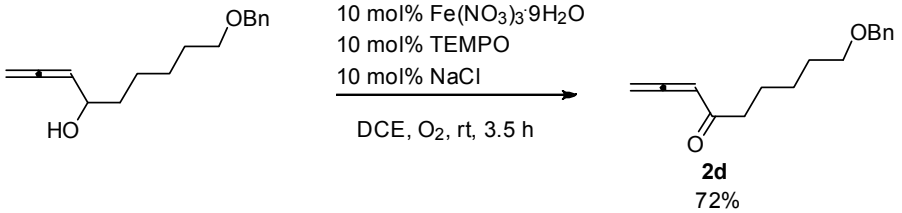
Entry	NHC precursor	t (h)	Product yield[b]%					Recovery of **2a**[b]%
			(*E*)-**3aa**	(*Z*)-**3aa**	**4aa**	**5aa**	Benzoin product	
1	**A1**	3	24	4	5	40[c]	—	—
2	**B1**	23	2	—	—	—	—	15
3	**B2**	22	3	—	—	—	—	22
4	**B3**	23.25	22	—	—	—	—	1
5	**C**	22	—	—	—	—	21	48
6	**D**	22	—	—	—	—	36	40
7	**E**	22	—	—	—	—	85	61
8	**F**	22	3	—	—	—	68	59

[a] Reaction conditions: A solution of NHC precursor and Cs_2CO_3 in dioxane (1 mL) was stirred at 20 °C for 10 min, then 0.48 mmol of **1a**, 0.4 mmol of **2a**, and dioxane (1 mL) were added sequentially. The resulting mixture was then stirred at 20 °C for the time indicated in the Table. [b] Determined by NMR of the crude product using dibromomethane as the internal standard. [c] Dr was 95:5 as determined by NMR.



2. Preparation of 1,2-allenyl ketones 2d

(1) 9-(Benzyloxy)nona-1,2-dien-4-one (2d)[6] (mdk-9-109)

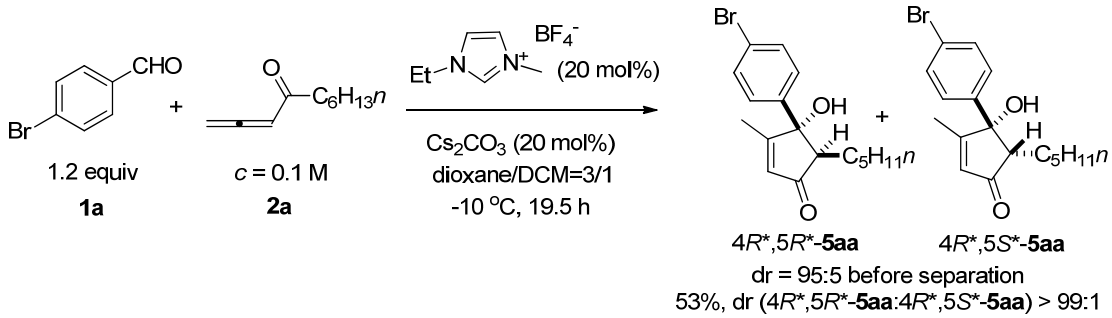


To a Schlenk flask were added $Fe(NO_3)_3 \cdot 9H_2O$ (124.2 mg, 0.3 mmol), TEMPO (48.0 mg, 0.3 mmol), NaCl (17.8 mg, 0.3 mmol), and DCE (8 mL) with stirring. Then 9-(benzyloxy)nona-1,2-dien-4-ol[7] (741.2 mg, 3 mmol) and DCE (4 mL) were added. The residual air in the reaction system was excluded by oxygen provided by a balloon.

After that, the resulting mixture was stirred at rt under oxygen provided by the balloon. After 3.5 h, the reaction was complete as monitored by TLC. Filtration through a short column of silica gel (eluent: ethyl ether (20 mL×3)), evaporation, and column chromatography on silica gel (petroleum ether (60- 90 ^{o}C)/ethyl acetate = 15/1 (480 mL) to 10/l (440 mL)) afforded **2d** (527.8 mg, 72%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.23 (m, 5H, ArH), 5.77 (t, *J* = 6.5 Hz, 1H, =CH), 5.22 (d, *J* = 6.3 Hz, 2H, =CH_2), 4.49 (s, 2H, CH_2), 3.46 (t, *J* = 6.6 Hz, 2H, CH_2), 2.61 (t, *J* = 7.4 Hz, 2H, CH_2), 1.69-1.55 (m, 4H, CH_2 × 2), 1.46-1.33 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.6, 200.8, 138.5, 128.3, 127.6, 127.5, 96.7, 79.3, 72.9, 70.1, 39.0, 29.5, 25.8, 24.3; IR (neat) ν (cm^{-1}) 3087, 3064, 3029, 2988, 2936, 2859, 2793, 1958, 1933, 1682, 1496, 1454, 1409, 1363, 1308, 1204, 1158, 1104, 1028; MS (70 ev, EI) m/z (%) 244 (M^{+}, 0.43), 91 (100); Elemental analysis calcd (%) for $C_{16}H_{20}O_2$: C, 78.65, H, 8.25; Found: C, 78.44; H, 8.16.

3. Preparation of cyclopent-2-enone-4-ols 5aa-5ee

(1) 4-(4-Bromophenyl)-4-hydroxy-3-methyl-5-pentylcyclopent-2-enone (5aa) (mdk-9-019-2)

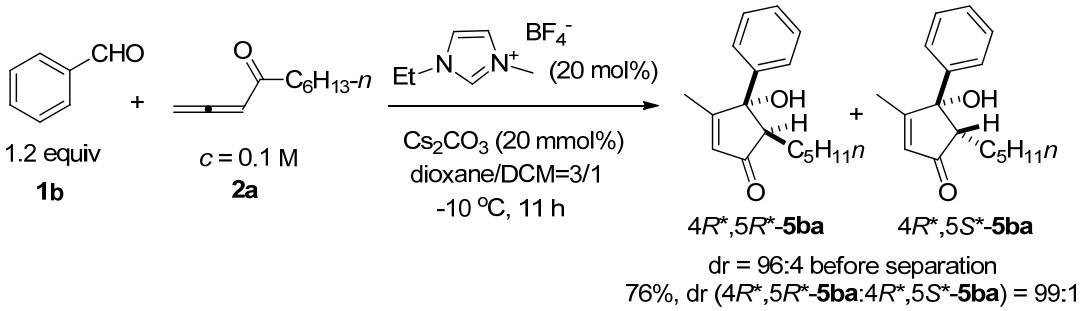


Typical Procedure I: To a dry Schlenk flask was added Cs_2CO_3 (65.1 mg, 0.2 mmol) under N_2. Then 1-ethyl-3-methylimidazolium tetrafluoroborate (40.3 mg, 0.2 mmol),

dioxane (3.75 mL), and CH_2Cl_2 (1.25 mL) were added sequentially under N_2. The resulting mixture was stirred at rt. After 10 min, the mixture was cooled to -10 ^oC, **1a** (226.8 mg, 1.2 mmol)/CH_2Cl_2 (1.25 mL) and **2a** (152.3 mg, 1 mmol)/dioxane (3.75 mL) were added sequentially. The resulting mixture was stirred at -10 ^oC. After 19.5 h, the reaction was complete as monitored by TLC. Filtration through a short column of silica gel (eluent: ethyl acetate (20 mL×3)), evaporation, and column chromatography on silica gel (petroleum ether (30 ^oC ~ 60 ^oC, redistillation)/ethyl acetate = 10/1 (440 mL) to 5/1 (480 mL × 2) to 3/1 (400 mL)) afforded **5aa** (0.1796 g, 53%, dr > 99:1) (the dr of the crude product was 95:5 as determined via the NMR analysis) as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J = 8.7 Hz, 2H, ArH), 7.13 (brs, 2H, ArH), 6.13 (q, J = 1.3 Hz, 1H, =CH), 2.72 (s, 1H, OH), 2.58 (dd, J_1 = 9.0 Hz, J_2 = 5.4 Hz, 1H, CH), 1.90 (d, J = 1.5 Hz, 3H, CH_3), 1.59-1.46 (m, 1H, one proton from CH_2), 1.40-0.94 (m, 6H, CH_2 × 3), 0.89-0.72 (m, 4H, CH_3 + one proton from CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.1, 176.1, 138.4, 131.3, 130.1, 127.5, 121.6, 85.2, 61.4, 31.6, 27.1, 25.9, 22.1, 13.9, 13.6; IR (neat) ν (cm^{-1}) 3435, 2954, 2930, 2859, 1693, 1625, 1589, 1572, 1487, 1466, 1456, 1434, 1397, 1375, 1307, 1297, 1245, 1232, 1205, 1164, 1075, 1010; MS (70 ev, EI) m/z (%) 338 (M^+(^{81}Br), 4.15), 336 (M^+(^{79}Br), 4.56), 265 (100); HRMS calcd for $C_{17}H_{21}{}^{79}BrO_2$ (M^+): 336.0725, found: 336.0728.

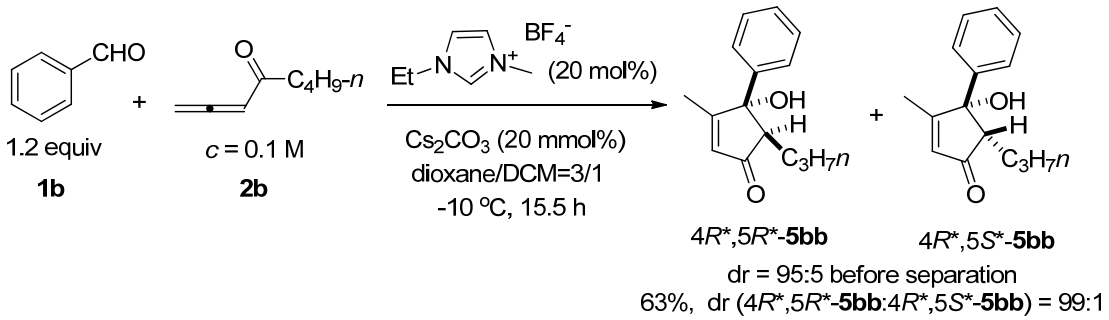
The following compounds were prepared according to **Typical procedure I**.

(2) 4-Hydroxy-3-methyl-5-pentyl-4-phenylcyclopent-2-enone (5ba) (mdk-8-065)



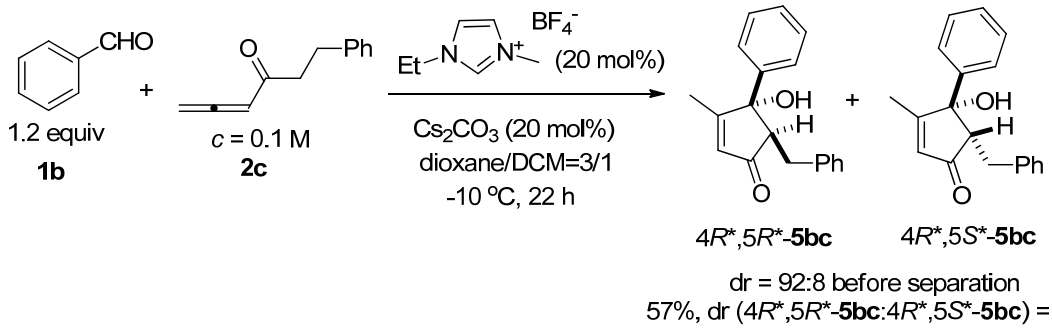
The reaction of **1b** (127.4 mg, 1.2 mmol), **2a** (153.0 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (40.0 mg, 0.2 mmol), and Cs_2CO_3 (65.3 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 ^oC for 11 h afforded **5ba** (0.1966 g, 76%, dr = 99:1) (petroleum ether (60 ^oC ~ 90 ^oC, redistillation)/ethyl acetate = 10/1 (440 mL) to 5/1 (480 mL) to 3/1 (400 mL)) (the dr of the crude product was 96:4 as determined via the NMR analysis) as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.51-6.97 (m, 5H, ArH), 6.14 (q, J = 1.3 Hz, 1H, =CH), 2.81 (s, 1H, OH), 2.60 (dd, J_1 = 9.2 Hz, J_2 = 5.3 Hz, 1H, CH), 1.91 (d, J = 1.5 Hz, 3H, CH_3), 1.59-1.45 (m, 1H, one proton from CH_2), 1.38-0.91 (m, 6H, CH_2 × 3), 0.90-0.78 (m, 1H, one proton from CH_2), 0.75 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.3, 176.1, 139.2, 130.1, 128.2, 127.5, 125.5, 85.6, 61.4, 31.7, 27.1, 25.8, 22.1, 13.9, 13.7; IR (neat) ν (cm^{-1}) 3439, 3087, 3060, 3028, 2955, 2930, 2859, 1693, 1626, 1601, 1491, 1448, 1374, 1301, 1246, 1232, 1205, 1165, 1131, 1093, 1066, 1015; MS (70 ev, EI) m/z (%) 258 (M^+, 14.47), 187 (100); Elemental analysis calcd (%) for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58; Found: C, 79.00; H, 8.81.

(3) 4-Hydroxy-3-methyl-4-phenyl-5-propylcyclopent-2-enone (5bb) (mdk-8-080)



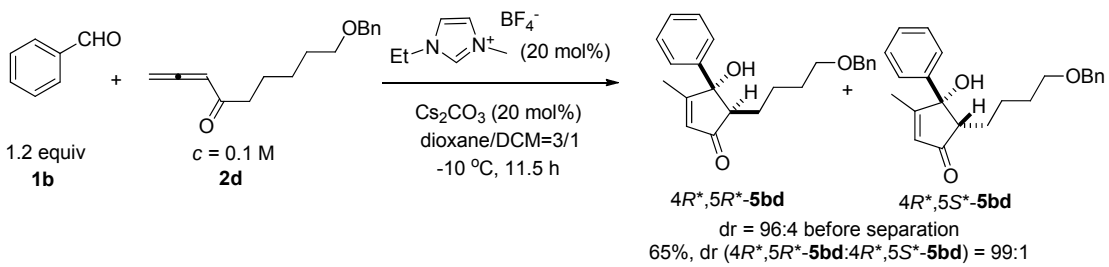
The reaction of **1b** (127.6 mg, 1.2 mmol), **2b** (124.3 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (39.9 mg, 0.2 mmol), and Cs_2CO_3 (65.1 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 ^oC for 15.5 h afforded **5bb** (0.1461 g, 63%, dr = 99:1) (petroleum ether (30 ^oC ~ 60 ^oC)/ethyl acetate = 10/1 (440 mL) to 5/1 (480 mL × 2 + 180 mL) to 3/1 (400 mL)) (the dr of the crude product was 95:5 as determined via the NMR analysis) as a liquid (solid, m. p. 79~81 °C (EtOH)): ^1H NMR (300 MHz, $CDCl_3$) δ 7.47-6.99 (m, 5H, ArH), 6.13 (q, J = 1.4 Hz, 1H, =CH), 3.18 (s, 1H, OH), 2.64 (dd, J_1 = 8.7 Hz, J_2 = 5.4 Hz, 1H, CH), 1.91 (d, J = 1.5 Hz, 3H, CH_3), 1.55-1.39 (m, 1H, one proton from CH_2), 1.39-1.14 (m, 2H, CH_2), 0.89-0.75 (m, 1H, one proton from CH_2), 0.69 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.7, 176.6, 139.3, 129.9, 128.2, 127.5, 125.5, 85.5, 61.1, 28.1, 20.8, 13.9, 13.7; IR (neat) ν (cm^{-1}) 3435, 3087, 3060, 3028, 2958, 2933, 2871, 1694, 1626, 1601, 1491, 1465, 1448, 1375, 1319, 1301, 1249, 1220, 1194, 1170, 1131, 1096, 1066, 1034, 1002; MS (70 ev, EI) m/z (%) 230 (M^+, 9.35), 187 (100); HRMS calcd for $C_{15}H_{18}O_2$ (M^+): 230.1307, found: 230.1310.

(4) 5-Benzyl-4-hydroxy-3-methyl-4-phenylcyclopent-2-enone (5bc) (mdk-8-098)



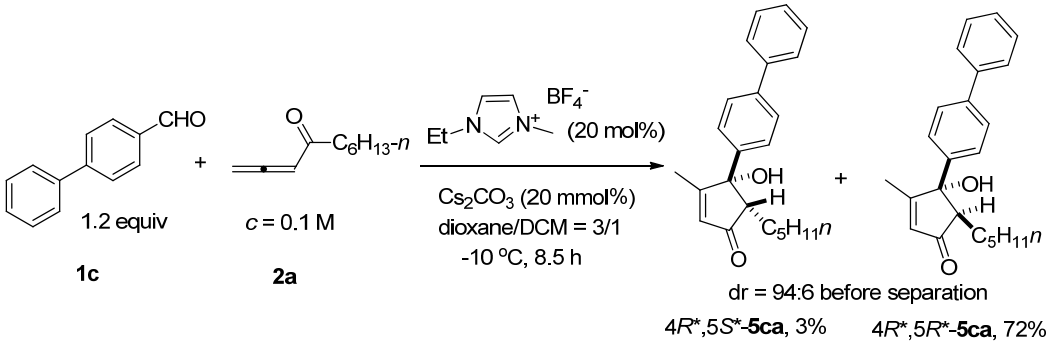
The reaction of **1b** (127.8 mg, 1.2 mmol), **2c** (173.0 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (40.1 mg, 0.2 mmol), and Cs_2CO_3 (65.1 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 ^oC for 22 h afforded **5bc** (0.1598 g, 57%, dr = 92:8) (petroleum ether (30 ^oC ~ 60 ^oC)/ethyl acetate = 10/1 (440 mL) to 5/1 (480 mL) to 3/1 (600 mL)) (the dr of the crude product was 92:8 as determined via the NMR analysis) as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.26 (m, 3H, ArH), 7.25-6.97 (m, 5H, ArH), 6.81-6.70 (m, 2H, ArH), [6.14 (q, J = 1.3 Hz, 0.92H), 6.12 (q, J = 1.2 Hz, 0.08H), 1H, =CH], 3.27-3.04 (m, 2H, CH_2), [2.42 (s, 0.08H), 2.30 (s, 0.83H), 1H, OH], 2.26-2.14 (m, 1H, CH), 1.90-1.82 (m, 3H, CH_3); IR (neat) ν (cm^{-1}) 3418, 3086, 3061, 3028, 2948, 2916, 2855, 1694, 1625, 1602, 1496, 1448, 1434, 1374, 1304, 1243, 1211, 1162, 1088, 1065, 1014; MS (70 ev, EI) m/z (%) 278 (M^+, 57.11), 187 (100); Elemental analysis calcd (%) for $C_{19}H_{18}O_2$: C, 81.99, H, 6.52; Found: C, 81.69; H, 6.47.

(5) 5-(4-(Benzyloxy)butyl)-4-hydroxy-3-methyl-4-phenylcyclopent-2-enone (5bd) (mdk-9-110)



The reaction of **1b** (128.0 mg, 1.2 mmol), **2d** (244.3 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (40.3 mg, 0.2 mmol), and Cs_2CO_3 (65.1 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 ^oC for 11.5 h afforded **5bd** (0.2337 g, 65%, purity= 98%, dr = 99:1) (petroleum ether (60 ^oC ~ 90 ^oC)/ethyl acetate = 10/1 (440 mL) to 5/1 (420 mL + 600 mL) to 3/1 (400 mL)) (the dr of the crude product was 96:4 as determined via the NMR analysis) as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.43-6.99 (m, 10H, ArH), 6.11 (q, J = 1.4 Hz, 1H, =CH), 4.42 (s, 2H, CH_2), 3.49-3.16 (m, 3H, OH + CH_2), 2.65 (dd, J_1 = 9.0 Hz, J_2 = 5.1 Hz, 1H, CH), 1.87 (d, J = 1.2 Hz, 3H, CH_3), 1.63-1.19 (m, 5H, CH_2 × 2 + one proton from CH_2), 1.01-0.82 (m, 1H, one proton from CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.5, 176.8, 139.3, 138.2, 129.6, 128.2, 128.1, 127.6, 127.44, 127.36, 125.5, 85.1, 72.6, 69.9, 60.9, 28.9, 25.4, 23.7, 13.6; IR (neat) ν (cm^{-1}) 3439, 3086, 3061, 3029, 2938, 2862, 2793, 1694, 1626, 1601, 1492, 1448, 1372, 1301, 1240, 1203, 1162, 1097, 1068, 1028; MS (70 ev, EI) m/z (%) 350 (M^+, 3.28), 91 (100); HRMS calcd for $C_{23}H_{26}O_3$ (M^+): 350.1882, found: 350.1878.

(6) (4*R,5*S**)-4-(4-Phenylphenyl)-4-hydroxy-3-methyl-5-pentylcyclopent-2-enone (4*R**,5*S**-5ca) (mdk-8-068-1) and (4*R**,5*R**)-4-(4-Phenylphenyl)-4-hydroxy-3-methyl-5-pentylcyclopent-2-enone (4*R**,5*R**-5ca) (mdk-8-068-2)**



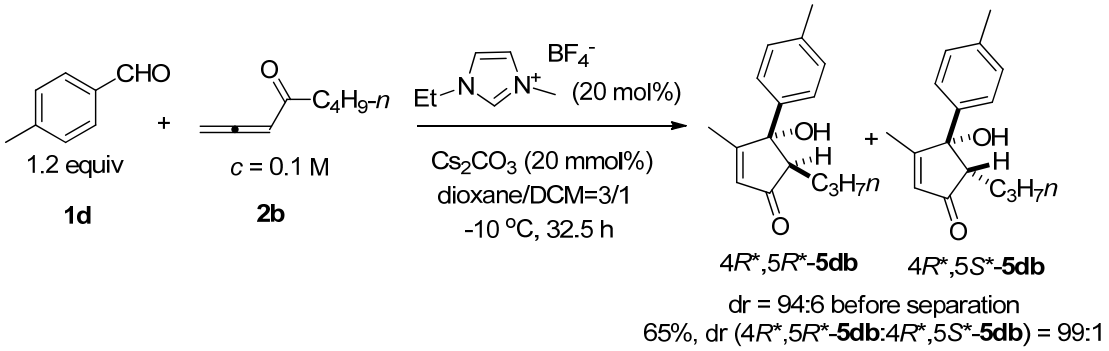
The reaction of **1c** (225.5 mg, 1.2 mmol), **2a** (152.9 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (40.0 mg, 0.2 mmol), and Cs_2CO_3 (65.5 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 ^oC for 8.5 h afforded impure 4*R**,5*S**-**5ca** (18.4 mg) and pure 4*R**,5*R**-**5ca** (241.0 mg, 72%) (petroleum ether (30 ^oC ~ 60 ^oC)/ethyl acetate = 10/1 (440 mL + 400 mL) to 5/1 (480 mL + 200 mL) to 3/1 (400 mL)) (the dr of the crude product was 94:6 as determined via the NMR analysis). Further purification of the impure 4*R**,5*S**-**5ca** by column chromatography on silica gel afforded pure 4*R**,5*S**-**5ca** (8.9 mg, 3%) (DCM (400 mL)).

4*R**,5*S**-**5ca**, minor, the less polar isomer, liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.62-7.57 (m, 4H, ArH), 7.49-7.34 (m, 5H, ArH), 6.10 (q, J = 1.3 Hz, 1H, =CH), 2.61 (dd, J_1 = 8.7 Hz, J_2 = 5.7 Hz, 1H, CH), 2.01 (s, 1H, OH), 1.92 (d, J = 1.5 Hz, 3H, CH_3), 1.83-1.59 (m, 2H, CH_2), 1.51-1.32 (m, 2H, CH_2), 1.31-1.14 (m, 4H, CH_2 × 2), 0.81 (t, J = 6.9 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.6, 177.2, 142.4, 140.4, 140.1, 130.5, 128.8, 127.4, 127.3, 127.0, 125.0, 82.8, 59.7, 31.8, 27.3, 26.8, 22.3, 14.1, 14.0; IR (neat) ν (cm^{-1}) 3444, 3057, 3029, 2954, 2927, 2857, 1694, 1626, 1600, 1486, 1435, 1405, 1374, 1298, 1263, 1213, 1195, 1180, 1133, 1076, 1007; MS (70 ev, EI) m/z (%) 334 (M^+, 14.35), 263 (100); HRMS calcd for $C_{23}H_{26}O_2$ (M^+): 334.1933, found: 334.1929.

4*R**,5*R**-**5ca**, major, the more polar isomer, liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.64-7.51 (m, 4H, ArH), 7.50-7.19 (m, 5H, ArH), 6.17 (q, J = 1.3 Hz, 1H, =CH), 2.66 (s, 1H, OH), 2.63 (dd, J_1 = 9.0 Hz, J_2 = 5.1 Hz, 1H, CH), 1.95 (d, J = 1.5 Hz, 3H,

CH_3), 1.64-1.49 (m, 1H, one proton from CH_2), 1.41-1.19 (m, 2H, CH_2), 1.19-0.83 (m, 5H, 2 × CH_2 + one proton from CH_2), 0.74 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.9, 177.0, 140.3, 140.1, 138.3, 129.8, 128.7, 127.3, 126.9, 126.7, 126.1, 85.3, 61.4, 31.6, 27.1, 25.9, 22.0, 13.82, 13.80; IR (neat) ν (cm^{-1}) 3448, 3057, 3029, 2953, 2929, 2858, 1691, 1625, 1600, 1560, 1486, 1435, 1404, 1374, 1317, 1301, 1267, 1232, 1207, 1196, 1180, 1164, 1132, 1076, 1007; MS (70 ev, EI) m/z (%) 334 (M^+, 18.23), 263 (100); HRMS calcd for $C_{23}H_{26}O_2$ (M^+): 334.1933, found: 334.1929.

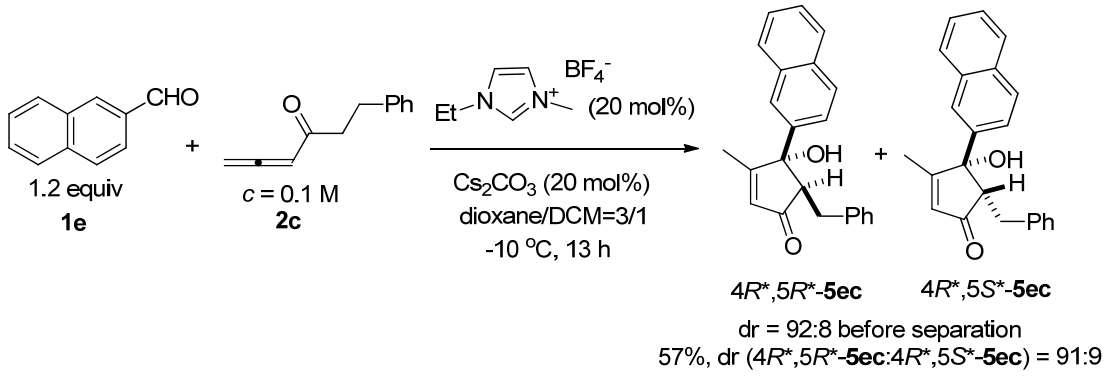
(7) 4-Hydroxy-3-methyl-5-propyl-4-(*p*-tolyl)cyclopent-2-enone (5db) (mdk-8-077)



The reaction of **1d** (145.0 mg, 1.2 mmol), **2b** (124.4 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (39.8 mg, 0.2 mmol), and Cs_2CO_3 (65.4 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 ^{o}C for 32.5 h afforded **5db** (0.1612 g, 65%, purity 98%, dr = 99:1) (petroleum ether (30 ^{o}C ~ 60 ^{o}C)/ethyl acetate = 10/1 (440 mL) to 5/1 (480 + 120 mL) to 3/1 (400 mL)) (the dr of the crude product was 94:6 as determined via the NMR analysis) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-6.77 (m, 4H, ArH), 6.11 (q, J = 1.3 Hz, 1H, =CH), 3.19 (s, 1H, OH), 2.63 (dd, J_1 = 8.7 Hz, J_2 = 5.4 Hz, 1H, CH), 2.34 (s, 3H, CH_3), 1.91 (d, J = 1.2 Hz, 3H, CH_3), 1.54-1.15 (m, 3H, CH_2 + one proton from CH_2), 0.93-0.76 (m, 1H, one proton from CH_2), 0.71 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 206.8, 176.8, 137.1, 136.3, 129.7, 128.9, 125.4, 85.4, 61.0, 28.0, 20.9, 20.8, 14.0, 13.7; IR (neat) ν (cm^{-1}) 3443, 3051, 3024, 2958, 2932, 2871, 1693, 1625, 1511, 1465, 1434, 1409, 1375, 1316, 1300, 1286, 1248, 1220, 1193, 1170, 1131, 1111, 1078, 1038, 1021, 1008; MS (70 ev, EI) m/z (%) 244 (M^+, 16.88), 201 (100); HRMS calcd for $C_{16}H_{20}O_2$ (M^+): 244.1463, found: 244.1472.

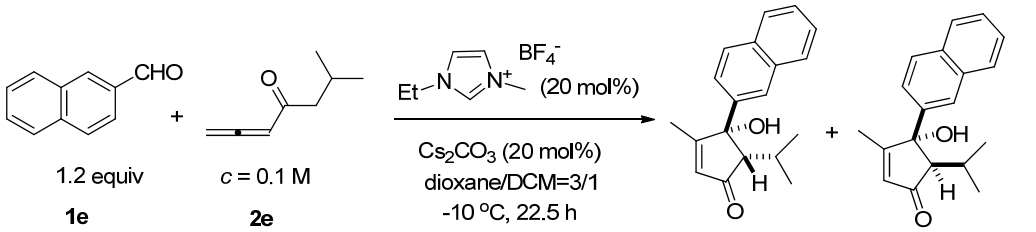
(8) 5-Benzyl-4-hydroxy-3-methyl-4-(naphth-2-yl)cyclopent-2-enone (5ec) (mdk-8-106)



The reaction of **1e** (191.5 mg, 1.2 mmol), **2c** (173.0 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (40.0 mg, 0.2 mmol), and Cs_2CO_3 (65.1 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 °C for 13 h afforded **5ec** (0.1866 g, 57%, dr = 91:9) (petroleum ether (30 °C ~ 60 °C)/ethyl acetate = 10/1 (440 mL) to 5/1 (480 mL + 180 mL) to 3/1 (400 mL + 200 mL)) (the dr of the crude product was 92:8 as determined via the NMR analysis) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92-7.59 (m, 4H, ArH), 7.59-7.40 (m, 2H, ArH), 7.20-6.90 (m, 4H, ArH), 6.81-6.57 (m, 2H, ArH), [6.20 (q, *J* = 1.3 Hz, 0.91H), 6.17 (q, *J* = 1.3 Hz, 0.09H), 1H, =CH], 3.30-3.06 (m, 2H, CH_2), [2.67 (s, 0.08H), 2.57 (s, 0.89H), 1H, OH], 2.22 (dd, J_1 = 14.4 Hz, J_2= 9.9 Hz, 1H, CH), 1.88 (d, *J* = 1.2 Hz, 3H, CH_3); IR (neat) ν (cm^{-1}) 3432, 3084, 3059, 3027, 2978, 2947, 2918, 2853, 1691, 1625,

1601, 1507, 1497, 1454, 1434, 1373, 1357, 1304, 1271, 1247, 1211, 1196, 1161, 1115, 1077, 1034, 1019; MS (70 ev, EI) m/z (%) 328 (M^+, 14.99), 237 (100); Elemental analysis calcd (%) for $C_{23}H_{20}O_2$: C, 84.12, H, 6.14; Found: C, 83.69; H, 6.25.

(9) (4*R,5*S**)-4-Hydroxy-5-isopropyl-3-methyl-4-(naphthalen-2-yl)cyclopent-2-enone (4*R**,5*S**-5ee) (mdk-8-115-1) and (4*R**,5*R**)-4-Hydroxy-5-isopropyl-3-methyl-4-(naphthalen-2-yl)cyclopent-2-enone (4*R**,5*R**-5ee) (mdk-8-115-2)**



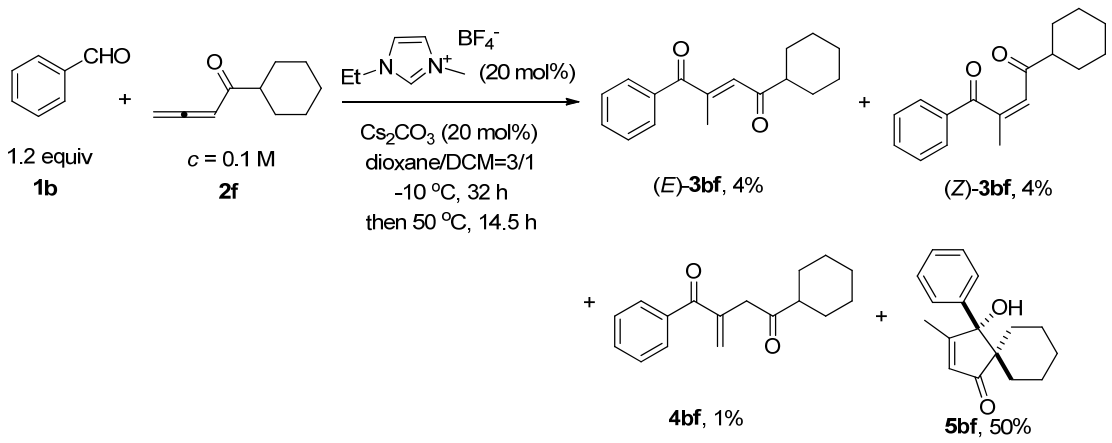
The reaction of **1e** (191.6 mg, 1.2 mmol), **2e** (124.5 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (39.9 mg, 0.2 mmol), and Cs_2CO_3 (65.1 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 ^oC for 22.5 h afforded 4*R**,5*S**-**5ee** (3.8 mg, 1%) and 4*R**,5*R**-**5ee** (156.3 mg, 55%) (petroleum ether (30 ^oC ~ 60 ^oC)/ethyl acetate = 60/1 (400 mL × 2) to 10/1 (440 mL) to 5/1 (480 mL × 3) to 3/1 (400 mL)) (the dr of the crude product was 95:5 as determined via the NMR analysis).

4*R**,5*S**-**5ee**, minor, the less polar isomer, liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.95-7.91 (m, 1H, ArH), 7.89-7.79 (m, 3H, ArH), 7.54-7.46 (m, 2H, ArH), 7.28 (dd, J_1 = 8.7 Hz, J_2 = 2.1 Hz, 1H, ArH), 6.14 (q, J = 1.3 Hz, 1H, =CH), 2.60 (d, J = 4.5 Hz, 1H, CH), 2.35-2.21 (m, 2H, one proton from CH_2 + OH), 1.89 (d, J = 1.5 Hz, 3H, CH_3), 1.11 (d, J = 6.6 Hz, 3H, CH_3), 1.06 (d, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (75

MHz, $CDCl_3$) δ 208.0, 177.1, 141.3, 133.1, 132.5, 131.7, 128.7, 128.1, 127.6, 126.5, 126.2, 123.3, 122.6, 83.6, 64.5, 27.8, 22.0, 19.8, 13.8; IR (neat) ν (cm^{-1}) 3445, 3057, 2957, 2929, 2872, 1688, 1628, 1599, 1507, 1466, 1435, 1385, 1368, 1296, 1272, 1231, 1199, 1160, 1132, 1078, 1020; MS (70 ev, EI) m/z (%) 280 (M^+, 10.47), 237 (100); HRMS calcd for $C_{19}H_{20}O_2$ (M^+): 280.1463, found: 280.1466.

4*R**,5*R**-**5ee**, major, the more polar isomer, solid, m. p. 147~149 °C (ethyl acetate): ^1H NMR (300 MHz, $CDCl_3$) δ 8.12-7.67 (m, 4H, ArH), 7.60-6.90 (m, 3H, ArH), 6.11 (q, *J* = 1.3 Hz, 1H, =CH), 2.56 (s, 1H, OH), 2.52 (d, *J* = 8.7 Hz, 1H, CH), 1.87 (d, *J* = 1.2 Hz, 3H, CH_3), 1.84-1.73 (m, 1H, CH), 1.04 (d, *J* = 6.6 Hz, 3H, CH_3), 0.73 (d, *J* = 6.6 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.7, 175.5, 137.3, 133.0, 132.5, 130.2, 128.2, 127.8, 127.5, 126.3, 126.2, 125.1, 123.7, 85.3, 67.4, 26.5, 21.8, 20.5, 13.3; IR (neat) ν (cm^{-1}) 3453, 3057, 2957, 2920, 2870, 1687, 1629, 1599, 1507, 1470, 1435, 1386, 1373, 1301, 1270, 1254, 1234, 1195, 1162, 1123, 1094, 1041, 1030; MS (70 ev, EI) m/z (%) 280 (M^+, 7.79), 237 (100); Elemental analysis calcd (%) for $C_{19}H_{20}O_2$: C, 81.40, H, 7.19; Found: C, 81.42; H, 7.24.

(10) 4-Hydroxy-3-methyl-4-phenylspiro[4.5]dec-2-en-1-one (5bf) (mdk-9-010-4)



The reaction of **1b** (126.9 mg, 1.2 mmol), **2f** (150.7 mg, 1 mmol),

1-ethyl-3-methylimidazolium tetrafluoroborate (40.0 mg, 0.2 mmol), and Cs_2CO_3 (65.0 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 ^oC for 32 h, then at 50 ^oC for 14.5 h afforded (*E*)-**3bf** (0.0094 g, 4%), **4bf** (0.0026 g, 1%), (*Z*)-**3bf** (0.0097 g, 4%), and **5bf** (0.1281 g, 50%) (in the order of polarity in silica gel column) (petroleum ether (60 ^oC ~ 90 ^oC, redistillation)/ethyl acetate = 40/1 (400 mL) to 30/1 (480 mL × 2 + 300 mL) to 10/1 (300 mL) to 5/1 (420 mL) to 3/1 (400 mL)).

(*E*)-**3bf**, the least polar isomer, liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.83-7.77 (m, 2H, ArH), 7.64-7.57 (m, 1H, ArH), 7.53-7.45 (m, 2H, ArH), 6.51 (q, *J* = 1.5 Hz, 1H, =CH), 2.45-2.31 (m, 4H, CH_3 + one proton from cyclohexyl group), 1.91-1.73 (m, 4H, from cyclohexyl group), 1.71-1.60 (m, 1H, from cyclohexyl group), 1.42-1.15 (m, 5H, from cyclohexyl group); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.6, 198.5, 149.3, 136.1, 133.1, 130.5, 129.7, 128.5, 51.8, 28.1, 25.8, 25.5, 15.8; IR (neat) ν (cm^{-1}) 2929, 2853, 1688, 1660, 1612, 1596, 1448, 1263, 1156, 1143, 1001; MS (70 ev, EI) m/z (%) 256 (M^+, 8.01), 83 (100); HRMS calcd for $C_{17}H_{20}O_2$ (M^+): 256.1463, found: 256.1465.

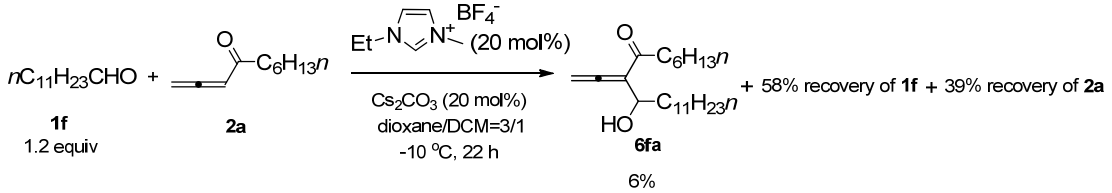
4bf, the less polar isomer, liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.87-7.80 (m, 2H, ArH), 7.57-7.50 (m, 1H, ArH), 7.48-7.40 (m, 2H, ArH), 5.89 (d, *J* = 0.9 Hz, 1H, one proton from $=CH_2$), 5.77 (s, 1H, one proton from $=CH_2$), 3.68 (d, *J* = 0.3 Hz, 2H, CH_2), 2.53-2.41 (m, 1H, from cyclohexyl group), 1.98-1.62 (m, 5H, from cyclohexyl group), 1.46-1.16 (m, 5H, from cyclohexyl group); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.9, 197.4, 142.3, 137.4, 132.2, 129.8, 128.7, 128.1, 50.7, 44.5, 28.4, 25.8, 25.6; IR (neat) ν (cm^{-1}) 2929, 2853, 1707, 1656, 1598, 1448, 1339, 1317, 1213, 1143, 1068; MS (70 ev, EI) m/z (%) 256 (M^+, 4.98), 83 (100); HRMS calcd for $C_{17}H_{20}O_2$ (M^+):

256.1463, found: 256.1463.

(*Z*)-**3bf**, the more polar isomer, liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89-7.81 (m, 2H, ArH), 7.59-7.50 (m, 1H, ArH), 7.49-7.41 (m, 2H, ArH), 6.44 (q, *J* = 1.5 Hz, 1H, =CH), 2.42-2.29 (m, 1H, from cyclohexyl group), 2.12 (d, *J* = 1.5 Hz, 3H, CH_3), 1.88-1.59 (m, 5H, from cyclohexyl group), 1.33-1.09 (m, 5H, from cyclohexyl group); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.0, 199.4, 154.1, 134.4, 133.2, 128.7, 128.3, 125.3, 50.1, 27.9, 25.7, 25.5, 21.7; IR (neat) ν (cm^{-1}) 2929, 2854, 1675, 1615, 1583, 1449, 1372, 1355, 1311, 1246, 1231, 1161, 1093, 1071; MS (70 ev, EI) m/z (%) 256 (M^+, 7.51), 174 (100); HRMS calcd for $C_{17}H_{20}O_2$ (M^+): 256.1463, found: 256.1466.

5bf, the most polar isomer, liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72-6.67 (m, 5H, ArH), 6.13 (q, *J* = 1.4 Hz, 1H, =CH), 2.51 (brs, 1H, OH), 1.92 (d, *J* = 1.5 Hz, 3H, CH_3), 1.85-1.40 (m, 6H, from cyclohexyl group), 1.38-1.06 (m, 3H, from cyclohexyl group), 0.91-0.78 (m, 1H, from cyclohexyl group); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.5, 173.9, 140.6, 129.6, 128.0, 127.4, 125.9, 87.5, 56.3, 32.9, 30.0, 25.4, 22.4, 21.6, 14.1; IR (neat) ν (cm^{-1}) 3462, 3085, 3058, 3027, 2933, 2861, 1686, 1631, 1600, 1490, 1449, 1374, 1361, 1310, 1266, 1226, 1194, 1147, 1127, 1105, 1069, 1031; MS (70 ev, EI) m/z (%) 256 (M^+, 77.01), 151 (100); HRMS calcd for $C_{17}H_{20}O_2$ (M^+): 256.1463, found: 256.1459.

(11) 9-Hydroxy-8-vinylideneicosan-7-one (6fa) (mdk-10-039)

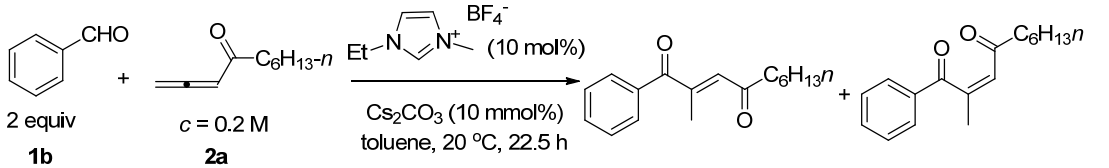


The reaction of **1f** (221.0 mg, 1.2 mmol), **2a** (152.3 mg, 1 mmol),

1-ethyl-3-methylimidazolium tetrafluoroborate (40.3 mg, 0.2 mmol), and Cs_2CO_3 (65.1 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 °C for 22 h afforded **6fa** (0.0192 g, 6%) (petroleum ether (60 °C ~ 90 °C)/ethyl acetate = 15/1 (300 mL) to 10/1 (300 mL)) (58% of **1f** and 39% of **2a** were recovered, respectively, as determined via NMR analysis) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.32 (d, J = 1.8 Hz, 2H, =CH_2), 4.49-4.38 (m, 1H, CH), 3.12 (d, J = 5.4 Hz, 1H, OH), 2.65 (dd, J_1 = 7.8 Hz, J_2 = 6.9 Hz, 2H, CH_2), 1.65-1.52 (m, 4H, CH_2 × 2), 1.36-1.19 (m, 24H, CH_2 × 12), 0.88 (t, J = 6.8 Hz, 6H, CH_3 × 2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.5, 203.2, 110.7, 81.2, 68.8, 39.8, 35.1, 31.9, 31.5, 29.7, 29.63, 29.62, 29.58, 29.4, 29.3, 28.8, 25.8, 24.7, 22.7, 22.5, 14.1, 14.0; IR (neat) ν (cm^{-1}) 3472, 2955, 2924, 2854, 1958, 1931, 1673, 1466, 1405, 1378, 1278, 1234, 1177, 1080, 1019; MS (70 ev, EI) m/z (%) 336 (M^+, 1.87), 43 (100); HRMS calcd for $C_{22}H_{40}O_2$ (M^+): 336.3028, found: 336.3026.

4. Mechanistic studies

(1) Preparation of (*E*)-3ba and (*Z*)-3ba (mdk-10-022)



To a dry Schlenk flask was added Cs_2CO_3 (97.8 mg, 0.3 mmol) under N_2. Then 1-ethyl-3-methylimidazolium tetrafluoroborate (60.9 mg, 0.3 mmol) and toluene (7.5 mL) were added sequentially under N_2. The resulting mixture was stirred at rt. After 10 min, the mixture was cooled to 20 °C, **1b** (636.4 mg, 6 mmol)/toluene (4.5 mL)

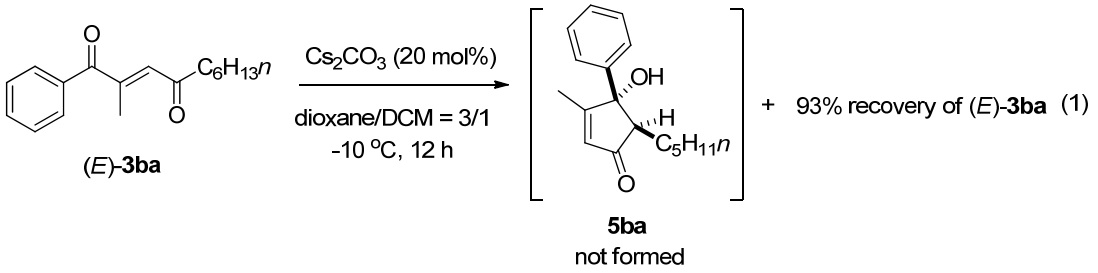
and **2a** (456.0 mg, 3 mmol)/toluene (3 mL) were added sequentially. Then the resulting mixture was stirred at 20 ^{o}C. After 22.5 h, the reaction was complete as monitored by TLC. Filtration through a short column of silica gel (eluent: ethyl acetate (20 mL×3)), evaporation, and column chromatography on silica gel (petroleum ether (60 ^{o}C ~ 90 ^{o}C)/ethyl acetate = 80/1 (400 mL × 4) to 40/1 (400 mL × 2) to 20/1 (420 mL × 2)) afforded (*E*)-**3ba** (0.2137 g, 27%, purity = 98%) and (*Z*)-**3ba** (0.0265 g, 3%, purity = 80%)

(*E*)-**3ba**, the less polar isomer, liquid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83-7.76 (m, 2H, ArH), 7.62-7.57 (m, 1H, ArH), 7.51-7.45 (m, 2H, ArH), 6.45 (q, *J* = 1.2 Hz, 1H, =CH), 2.51 (t, *J* = 7.5 Hz, 2H, CH_2), 2.36 (d, *J* = 1.2 Hz, 3H, CH_3), 1.64-1.57 (m, 2H, CH_2), 1.34-1.23 (m, 6H, CH_2 × 3), 0.88 (t, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.7, 198.4, 148.8, 135.9, 133.1, 130.8, 129.7, 128.5, 44.8, 31.5, 28.7, 23.7, 22.4, 15.7, 14.0; IR (neat) ν (cm^{-1}) 3061, 3027, 2956, 2929, 2857, 1694, 1661, 1615, 1597, 1579, 1448, 1405, 1377, 1361, 1316, 1265, 1209, 1179, 1155, 1130, 1075, 1031, 1003; MS (70 ev, EI) m/z (%) 258 (M^+, 38.90), 105 (100); HRMS calcd for $C_{17}H_{22}O_2$ (M^+): 258.1620, found: 258.1621.

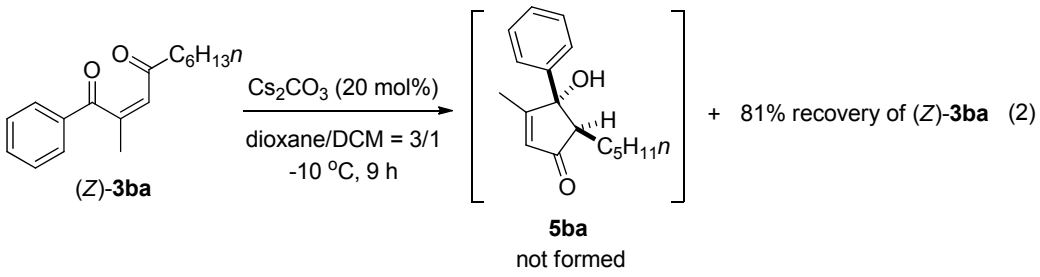
(*Z*)-**3ba**, the more polar isomer, liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90-7.83 (m, 2H, ArH), 7.60-7.52 (m, 1H, ArH), 7.50-7.40 (m, 2H, ArH), 6.37 (q, *J* = 1.5 Hz, 1H, =CH), 2.44 (t, *J* = 7.4 Hz, 2H, CH_2), 2.12 (d, *J* = 1.5 Hz, 3H, CH_3), 1.56-1.43 (m, 2H, CH_2), 1.28-1.13 (m, 6H, CH_2 × 3), 0.84 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.4, 198.5, 153.7, 134.4, 133.3, 128.7, 128.3, 126.1, 42.9, 31.5, 28.7, 23.6, 22.4, 21.6, 14.0; IR (neat) ν (cm^{-1}) 2955, 2929, 2857, 1674, 1615, 1583,

1449, 1405, 1370, 1310, 1239, 1159, 1123, 1076; MS (70 ev, EI) m/z (%) 258 (M^+, 6.39), 105 (100); HRMS calcd for $C_{17}H_{22}O_2$ (M^+): 258.1620, found: 258.1623.

(2) Reactions of (*E*)-3ba and (*Z*)-3ba in the presence of Cs_2CO_3 respectively

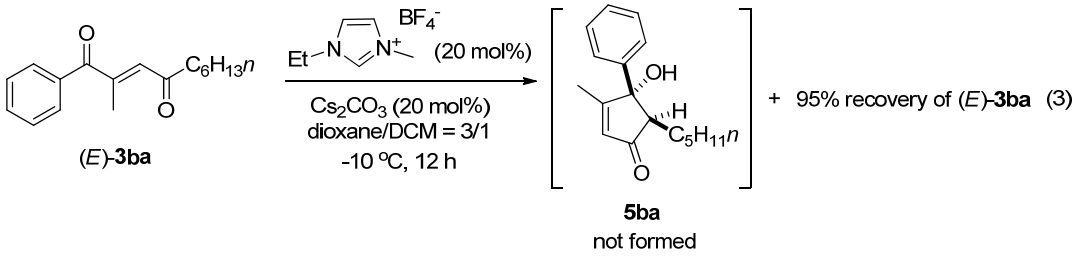


To a dry Schlenk tube was added Cs_2CO_3 (13.2 mg, 0.04 mmol) under N_2. Then dioxane (0.75 mL) and CH_2Cl_2 (0.25 mL) were added sequentially under N_2. The mixture was cooled to -10 °C, (*E*)-**3ba** (51.5 mg, 0.2 mmol, purity = 98%), CH_2Cl_2 (0.25 mL), and dioxane (0.75 mL) were added sequentially. The resulting mixture was stirred at -10 °C. After 12 h, the reaction mixture was filtrated through a short column of silica gel (eluent: ethyl acetate (15 mL×3)), evaporated, and analyzed by NMR with 7 μL of CH_2Br_2 as the internal standard. As a result, 93% of (*E*)-**3ba** was recovered and **5ba** was not formed.

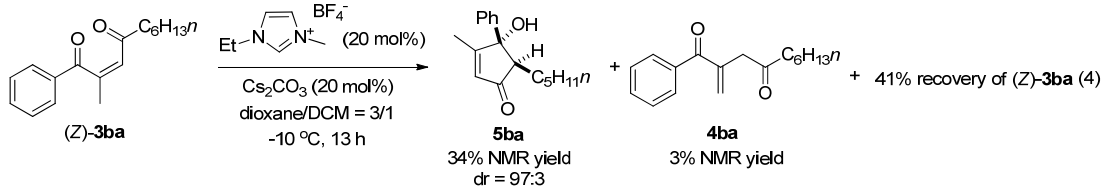


Following the procedure for eq (1), the reaction of (*Z*)-**3ba (**26.0 mg**,** 0.08 mmol**,** purity = 80%**)** and Cs_2CO_3 (5.3 mg, 0.016 mmol) in dioxane (0.6 mL) and CH_2Cl_2 (0.2 mL) at -10 °C for 9 h afforded 81% recovery of (*Z*)-**3ba** without the formation of **5ba** as determined by NMR analysis.

(3) Reactions of (*E*)-3ba and (*Z*)-3ba in the presence of 1-ethyl-3-methylimidazolium tetrafluoroborate and Cs_2CO_3 respectively



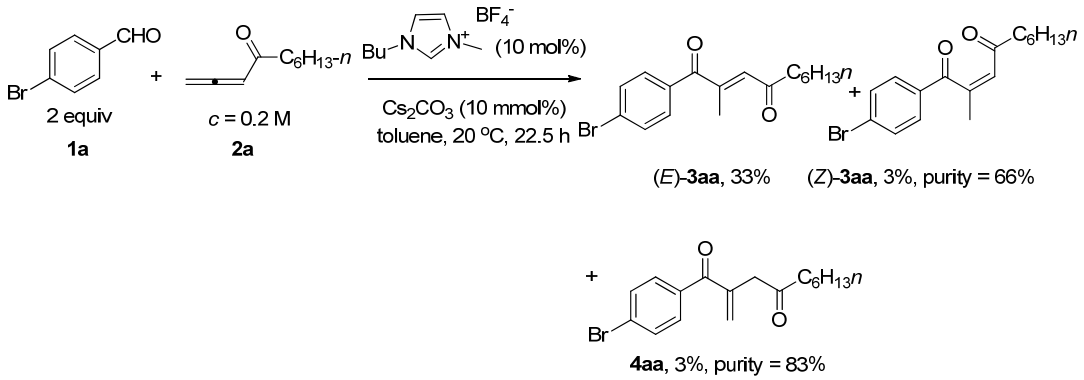
To a dry Schlenk tube was added Cs_2CO_3 (13.1 mg, 0.04 mmol) under N_2. Then 1-ethyl-3-methylimidazolium tetrafluoroborate (8.0 mg, 0.04 mmol), dioxane (0.75 mL), and CH_2Cl_2 (0.25 mL) were added sequentially under N_2. The resulting mixture was stirred at rt. After 10 min, the mixture was cooled to -10 °C, (*E*)-**3ba** (52.3 mg, 0.2 mmol, purity = 98%), CH_2Cl_2 (0.25 mL), and dioxane (0.75 mL) were added sequentially. The resulting mixture was stirred at -10 °C. After 12 h, the reaction mixture was filtrated through a short column of silica gel (eluent: ethyl acetate (15 mL×3)), evaporated, and analyzed by NMR with 7 μL of CH_2Br_2 as the internal standard. As a result, 95% of (*E*)-**3ba** was recovered and the formation of **5ba** was not observed.



Following the procedure for eq (3), the reaction of (*Z*)-**3ba** (20.8 mg, 0.064 mmol, purity = 80%), 1-ethyl-3-methylimidazolium tetrafluoroborate (2.7 mg, 0.0128 mmol), Cs_2CO_3 (4.3 mg, 0.0128 mmol) in dioxane (0.48 mL), and CH_2Cl_2 (0.16 mL) at -10 °C for 13 h afforded 34% of **5ba**, 3% of **4ba**, and 41% recovery of (*Z*)-**3ba** as

determined by NMR analysis.

5. Preparation of (*E*)-3aa, 4aa, and (*Z*)-3aa (mdk-10-084)



To a dry Schlenk flask was added Cs_2CO_3 (12.9 mg, 0.04 mmol) under N_2. Then 1-butyl-3-methylimidazolium tetrafluoroborate (9.1 mg, 0.04 mmol) and toluene (1 mL) were added sequentially under N_2. The resulting mixture was stirred at 20 ^oC. After 10 min, **1a** (151.6 mg, 0.8 mmol), **2a** (60.5 mg, 0.4 mmol), and toluene (1 mL) were added sequentially. Then the resulting mixture was stirred at 20 ^oC. After 22.5 h, the reaction was complete as monitored by TLC. Filtration through a short column of silica gel (eluent: ethyl ether (10 mL×3)), evaporation, and column chromatography on silica gel (petroleum ether (60 ^oC ~ 90 ^oC, redistillation)/ethyl acetate = 80/1 (400 mL × 2) to 60/1 (420 mL) to 40/1 (400 mL) to 20/1 (420 mL)) afforded (*E*)-**3aa** (0.0442 g, 33%), **4aa** (0.0048 g, 3%, purity = 83%), and (*Z*)-**3aa** (0.0042 g, 3%, purity = 66%) (in the order of polarity in silica gel column)

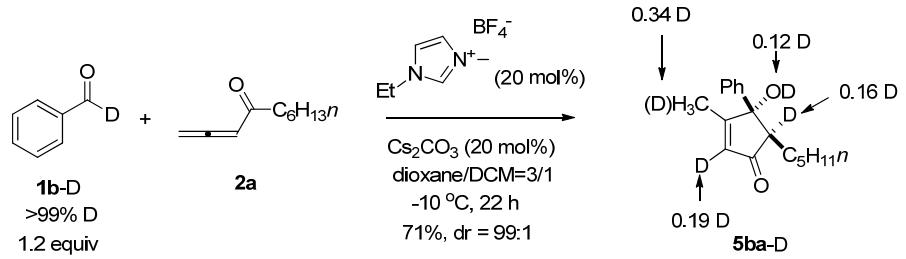
(*E*)-**3aa**, the less polar isomer, liquid: ^1H NMR (600 MHz, $CDCl_3$) δ 7.69-7.65 (m, 2H, ArH), 7.64-7.61 (m, 2H, ArH), 6.42 (q, *J* = 1.2 Hz, 1H, =CH), 2.51 (t, *J* = 7.5 Hz, 2H, CH_2), 2.34 (d, *J* = 1.2 Hz, 3H, CH_3), 1.64-1.57 (m, 2H, CH_2), 1.34-1.24 (m, 6H, CH_2 × 3), 0.88 (t, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.6,

197.4, 148.4, 134.7, 131.9, 131.1, 128.3, 44.8, 31.5, 28.8, 23.7, 22.4, 15.6, 14.0; IR (neat) ν (cm^{-1}) 2955, 2929, 2857, 1694, 1667, 1661, 1615, 1585, 1567, 1481, 1464, 1456, 1396, 1378, 1304, 1261, 1177, 1155, 1130, 1109, 1069, 1008; MS (70 ev, EI) m/z (%) 338 (M^+(^{81}Br), 12.47), 336 (M^+(^{79}Br), 12.56), 113 (100); HRMS calcd for $C_{17}H_{21}{}^{79}BrO_2$ (M^+): 336.0725, found: 336.0718.

4aa, the "middle" isomer, liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.68 (m, 2H, ArH), 7.62-7.56 (m, 2H, ArH), 5.90 (s, 1H, one proton from $=CH_2$), 5.72 (s, 1H, one proton from $=CH_2$), 3.63 (s, 2H, CH_2), 2.51 (t, *J* = 7.5 Hz, 2H, CH_2), 1.64-1.51 (m, 2H, CH_2), 1.36-1.19 (m, 6H, CH_2 × 3), 0.87 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.9, 196.3, 142.0, 136.0, 131.5, 131.3, 128.6, 127.3, 46.5, 42.7, 31.6, 28.8, 23.6, 22.5, 14.0; IR (neat) ν (cm^{-1}) 2955, 2929, 2857, 1715, 1660, 1585, 1483, 1466, 1397, 1338, 1215, 1174, 1127, 1069, 1012; MS (70 ev, EI) m/z (%) 338 (M^+(^{81}Br), 15.50), 336 (M^+(^{79}Br), 14.57), 43 (100); HRMS calcd for $C_{17}H_{21}{}^{79}BrO_2$ (M^+): 336.0725, found: 336.0729.

(*Z*)-**3aa**, the more polar isomer, liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76-7.68 (m, 2H, ArH), 7.63-7.54 (m, 2H, ArH), 6.37 (q, *J* = 1.6 Hz, 1H, =CH), 2.44 (t, *J* = 7.4 Hz, 2H, CH_2), 2.10 (d, *J* = 1.2 Hz, 3H, CH_3), 1.56-1.44 (m, 2H, CH_2), 1.35-1.15 (m, 6H, CH_2 × 3), 0.85 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.5, 198.3, 153.1, 133.3, 132.1, 129.7, 128.4, 126.3, 42.9, 31.5, 28.8, 23.5, 22.4, 21.5, 14.0; IR (neat) ν (cm^{-1}) 2954, 2928, 2857, 1674, 1616, 1585, 1483, 1441, 1394, 1370, 1244, 1158, 1070, 1010; MS (70 ev, EI) m/z (%) 338 (M^+(^{81}Br), 9.91), 336 (M^+(^{79}Br), 9.01), 183 (100); HRMS calcd for $C_{17}H_{21}{}^{79}BrO_2$ (M^+): 336.0725, found: 336.0733.

6. The deuterium-labeling experiment (mdk-10-125)



The reaction of **1b-D**[8] (129.0 mg, 1.2 mmol, >99% D), **2a** (152.5 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (40.6 mg, 0.2 mmol), and Cs_2CO_3 (65.3 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 ^oC for 22 h afforded **5ba-D** (184.5 mg, 71%, dr = 99:1) (petroleum ether (60 ^oC ~ 90 ^oC, redistillation)/ethyl acetate = 10/1 (440 mL) to 5/1 (480 mL)) (the dr of the crude product was 96:4 as determined via the NMR analysis) as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.50-6.92 (m, 5H, ArH), 1.59-1.44 (m, 1H, one proton from CH_2), 1.39-0.90 (m, 6H, CH_2 × 3), 0.90-0.69 (m, 4H, one proton from CH_2 + CH_3); the following signal is discernible for **5ba**: [6.14 (q, J = 1.5 Hz, 0.80H), 6.07 (q, J = 1.2 Hz, 0.01H), 0.81H, =CH], 2.81 (s, 0.88H, OH), 2.60 (dd, J_1 = 8.9 Hz, J_2 = 5.3 Hz, 0.84H, CH), 1.93-1.86 (m, 2.66H, CH_3); IR (neat) ν (cm^{-1}) 3432, 3087, 3060, 3028, 2955, 2931, 2860, 1694, 1625, 1602, 1492, 1448, 1375, 1317, 1302, 1247, 1233, 1205, 1176, 1127, 1099, 1067; MS (70 ev, EI) m/z (%) 259 (M^+(D), 10.08), 258 (M^+, 12.72), 187 (100); HRMS calcd for $C_{17}H_{21}DO_2$ (M^+): 259.1683, found: 259.1681.

References:

1 S. Ma, S. Yu and S. Yin, *J. Org. Chem*., 2003, **68**, 8996.

2 B. Cazes and S. Julia, *Synth. Commun.*, 1977, **7**, 273.

3 A. Denichoux, F. Ferreira and F. Chemla, *Org. Lett*., 2004, **6**, 3509.

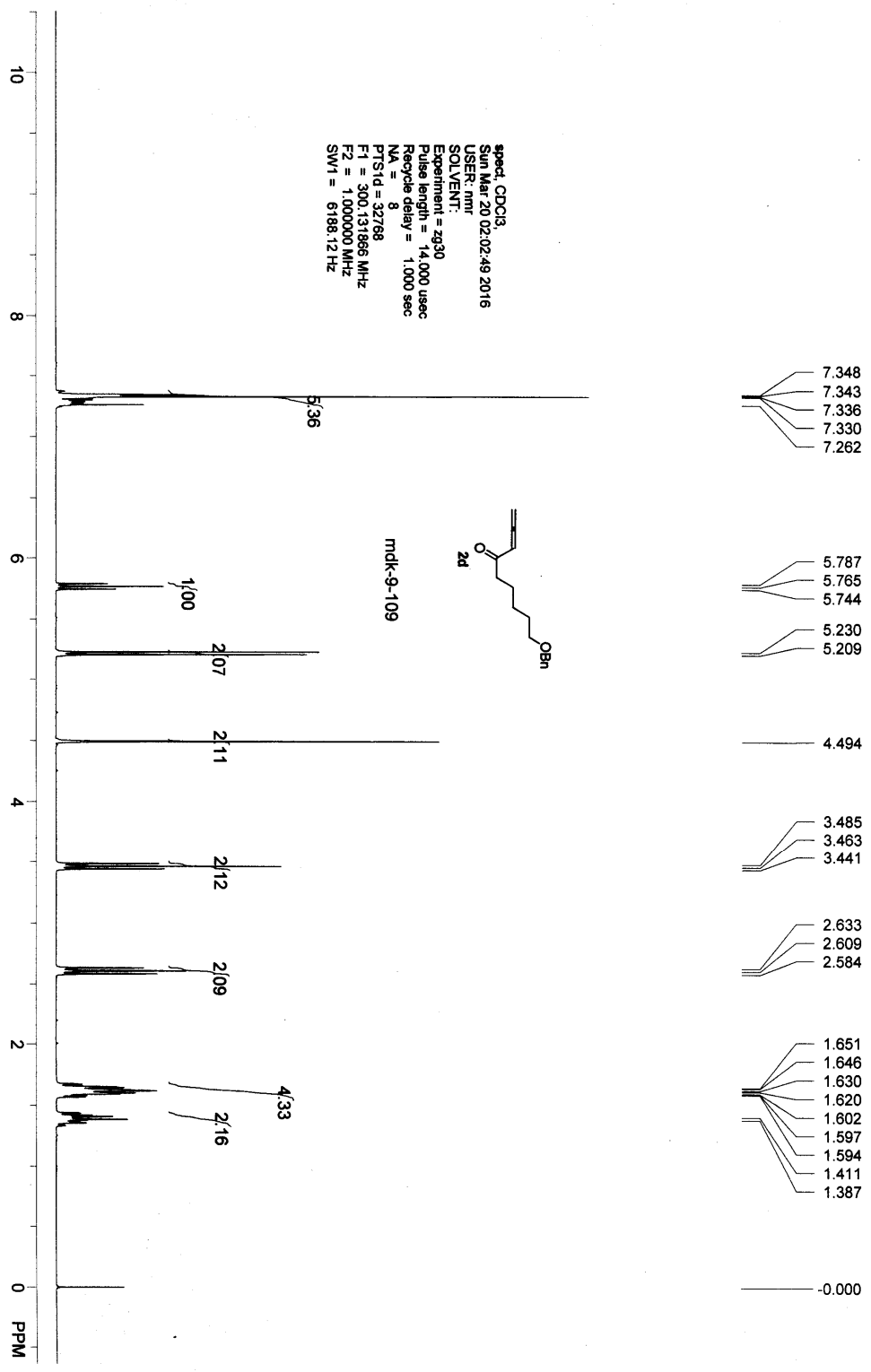
4 N. Jin, T. Misaki and T. Sugimura, *Chem. Lett*., 2013, **42**, 894.

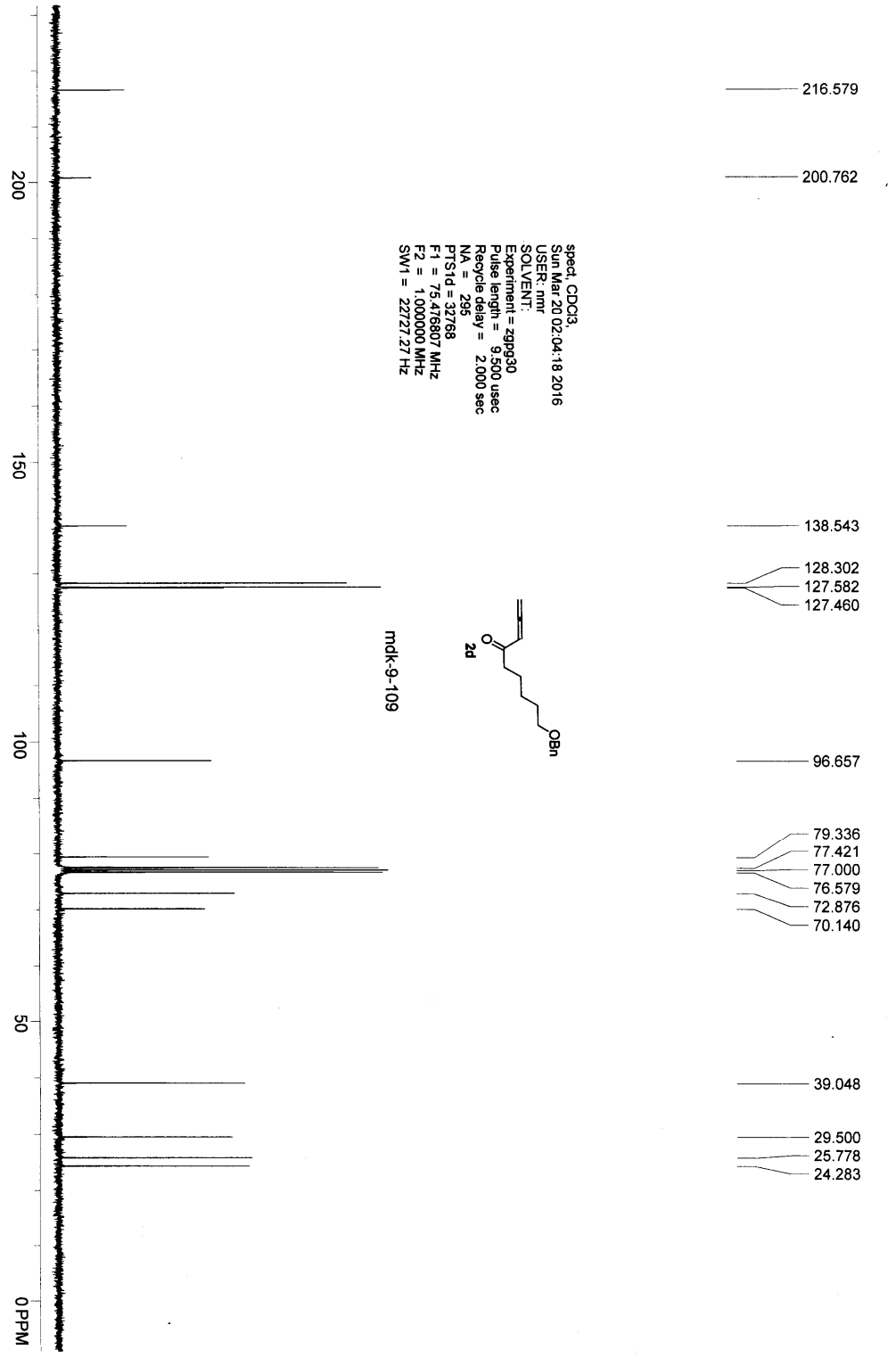
5 (a) L. O. Davis and S. L. Tobey, *Tetrahedron Lett*., 2010, **51**, 6078; (b) J. Liu and S. Ma, *Tetrahedron*, 2013, **69**, 10161.

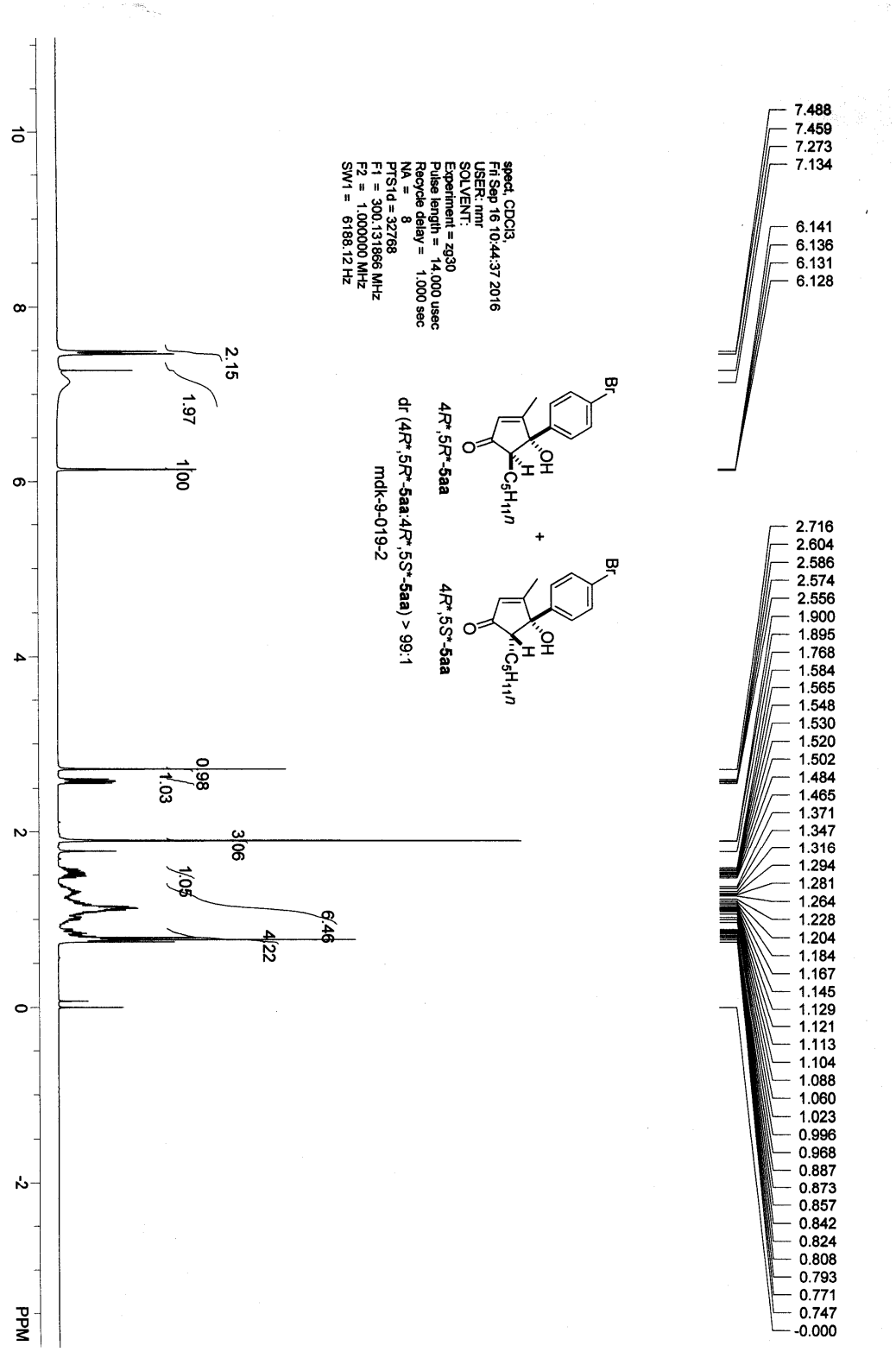
6 (a) S. Ma, J. Liu, S. Li, B. Chen, J. Cheng, J. Kuang, Y. Liu, B. Wan, Y. Wang, J. Ye, Q. Yu, W. Yuan and S. Yu, *Adv. Synth. Catal*., 2011, **353**, 1005; (b) *US Pat*., 8 748 669 B2, 2014; (c) *JP Pat*., 5 496 366 B2, 2014; (d) *EP Pat*., 2 599 765 B1, 2016.

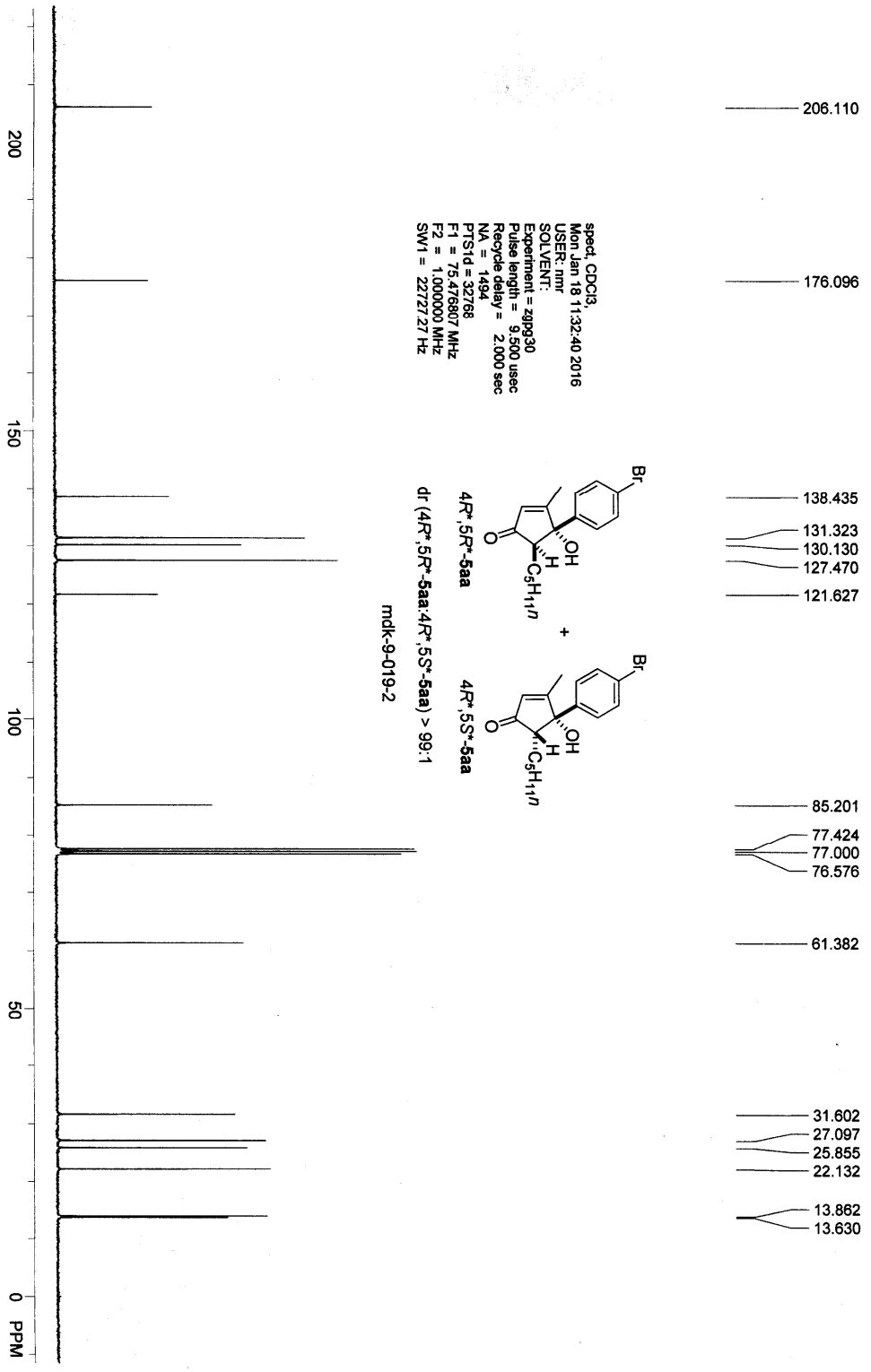
7 J. Kuang, H. Luo and S. Ma, *Adv. Synth. Catal*., 2012, **354**, 933.

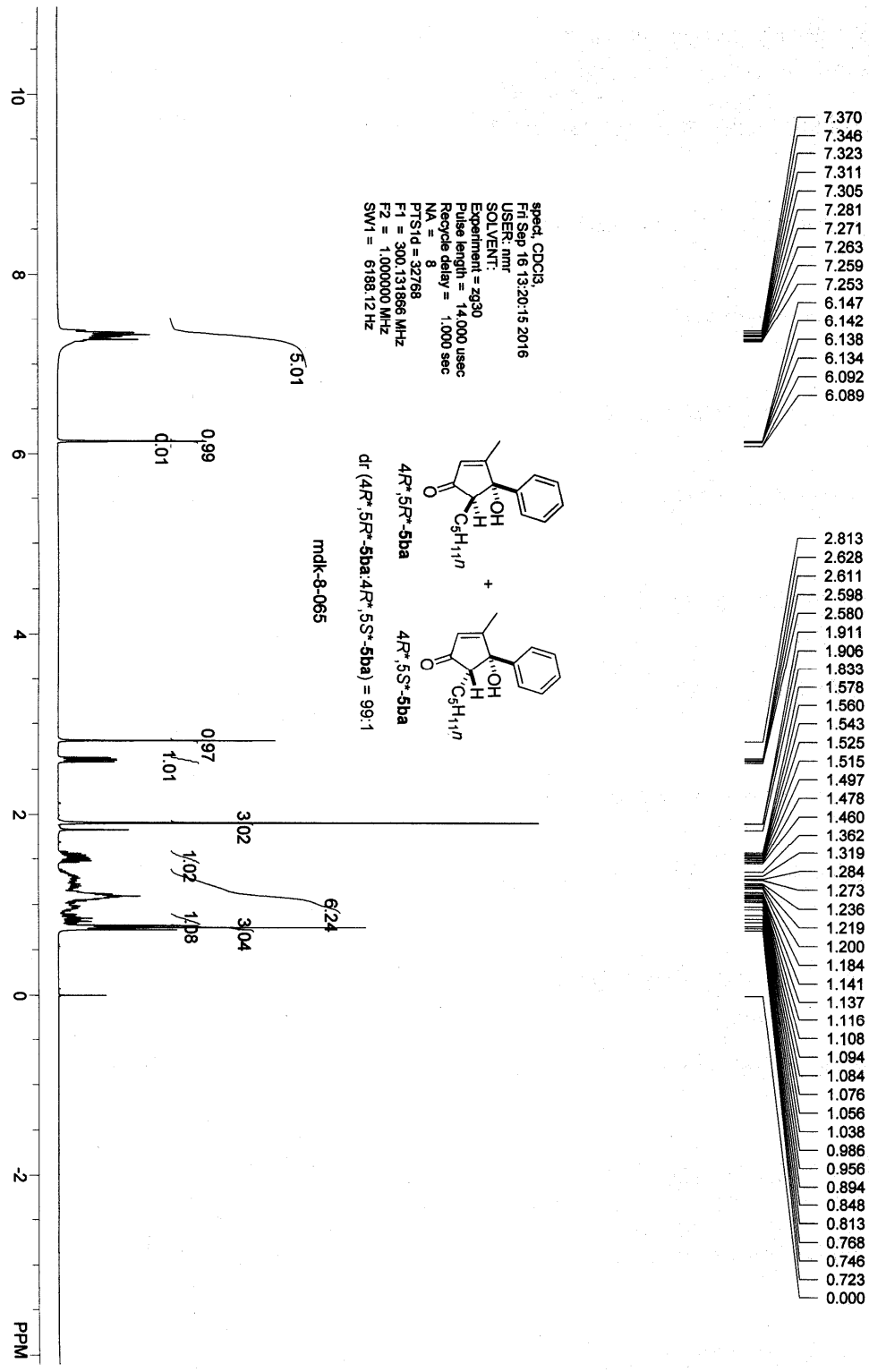
8 H. Yuan, W. Yoo, H. Miyamura and S. Kobayashi, *J. Am. Chem. Soc*., 2012, **134**, 13970.

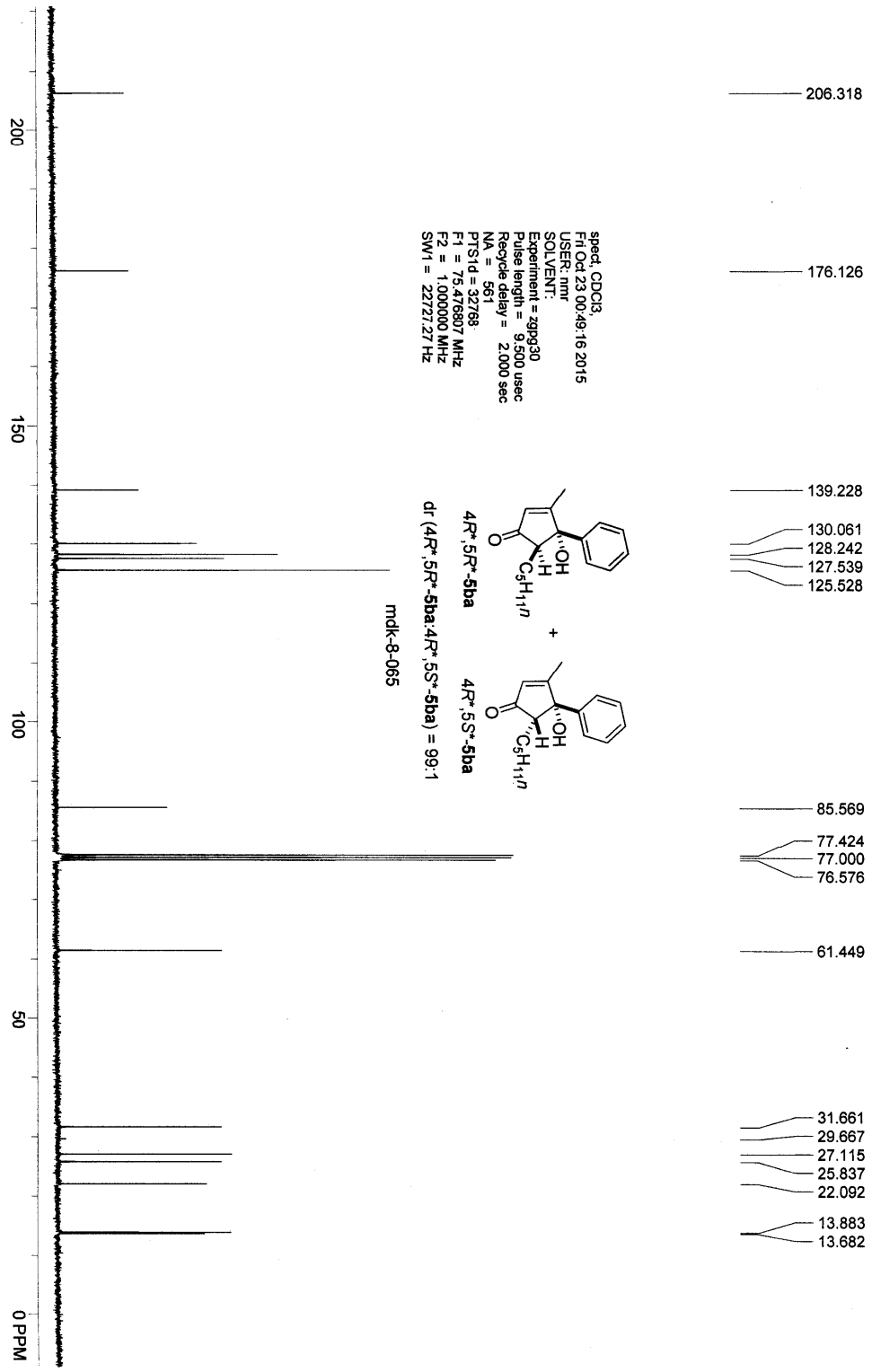

spect, CDCl3,
Sun Mar 20 02:02:49 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-9-109
2d
OBn
5.36
1.00
2.07
2.11
2.12
2.09
4.33
2.16
7.348
7.343
7.336
7.330
7.262
5.787
5.765
5.744
5.230
5.209
4.494
3.485
3.463
3.441
2.633
2.609
2.584
1.651
1.646
1.630
1.620
1.602
1.597
1.594
1.411
1.387
-0.000
10
8
6
4
2
0
PPM

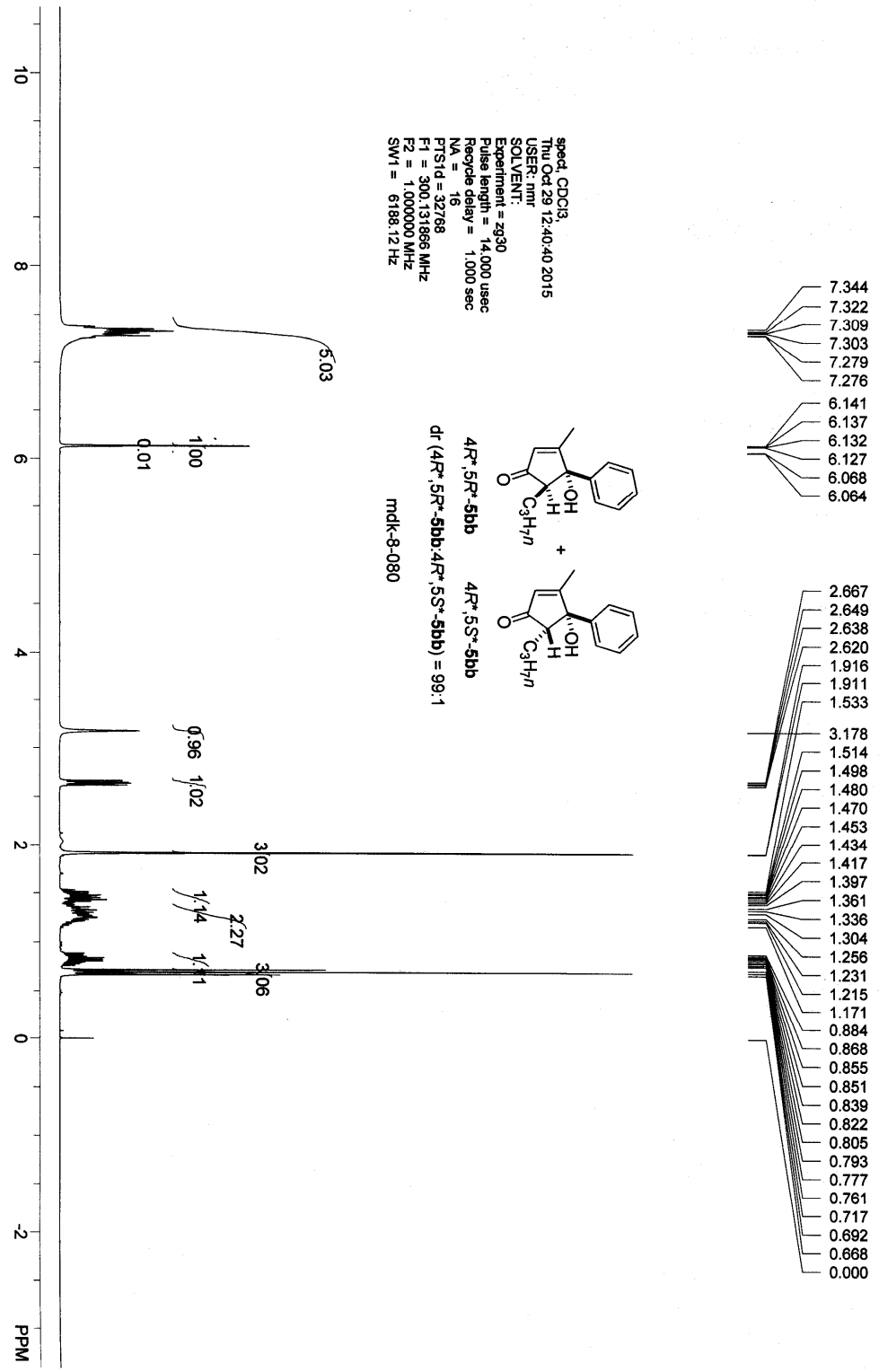

spect, CDCl3,
Sun Mar 20 02:04:18 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 295
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-9-109
2d
OBn
216.579
200.762
138.543
128.302
127.582
127.460
96.657
79.336
77.421
77.000
76.579
72.876
70.140
39.048
29.500
25.778
24.283
200
150
100
50
0 PPM

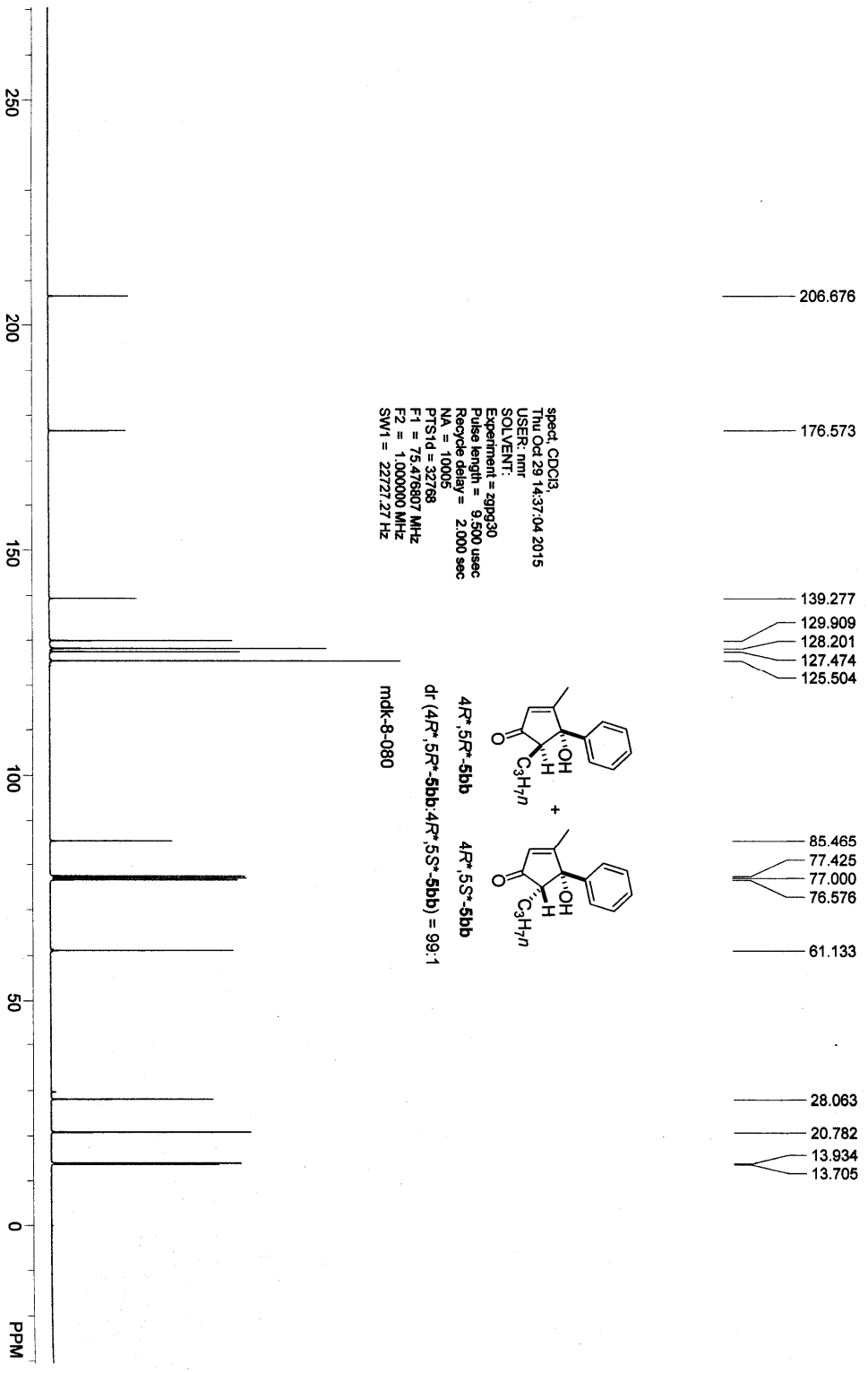

spect. CDCl3.
Fri Sep 16 10:44:37 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
4R*,5R*-5aa
+
4R*,5S*-5aa
dr (4R*,5R*-5aa:4R*,5S*-5aa) > 99:1
mdk-9-019-2
7.488
7.459
7.273
7.134
6.141
6.136
6.131
6.128
2.716
2.604
2.586
2.574
2.556
1.900
1.895
1.768
1.584
1.565
1.548
1.530
1.520
1.502
1.484
1.465
1.371
1.347
1.316
1.294
1.281
1.264
1.228
1.204
1.184
1.167
1.145
1.129
1.121
1.113
1.104
1.088
1.060
1.023
0.996
0.968
0.887
0.873
0.857
0.842
0.824
0.808
0.793
0.771
0.747
-0.000
2.15
1.97
1.00
0.98
1.03
3.06
1.05
6.46
4.22
10
8
6
4
2
0
-2
PPM

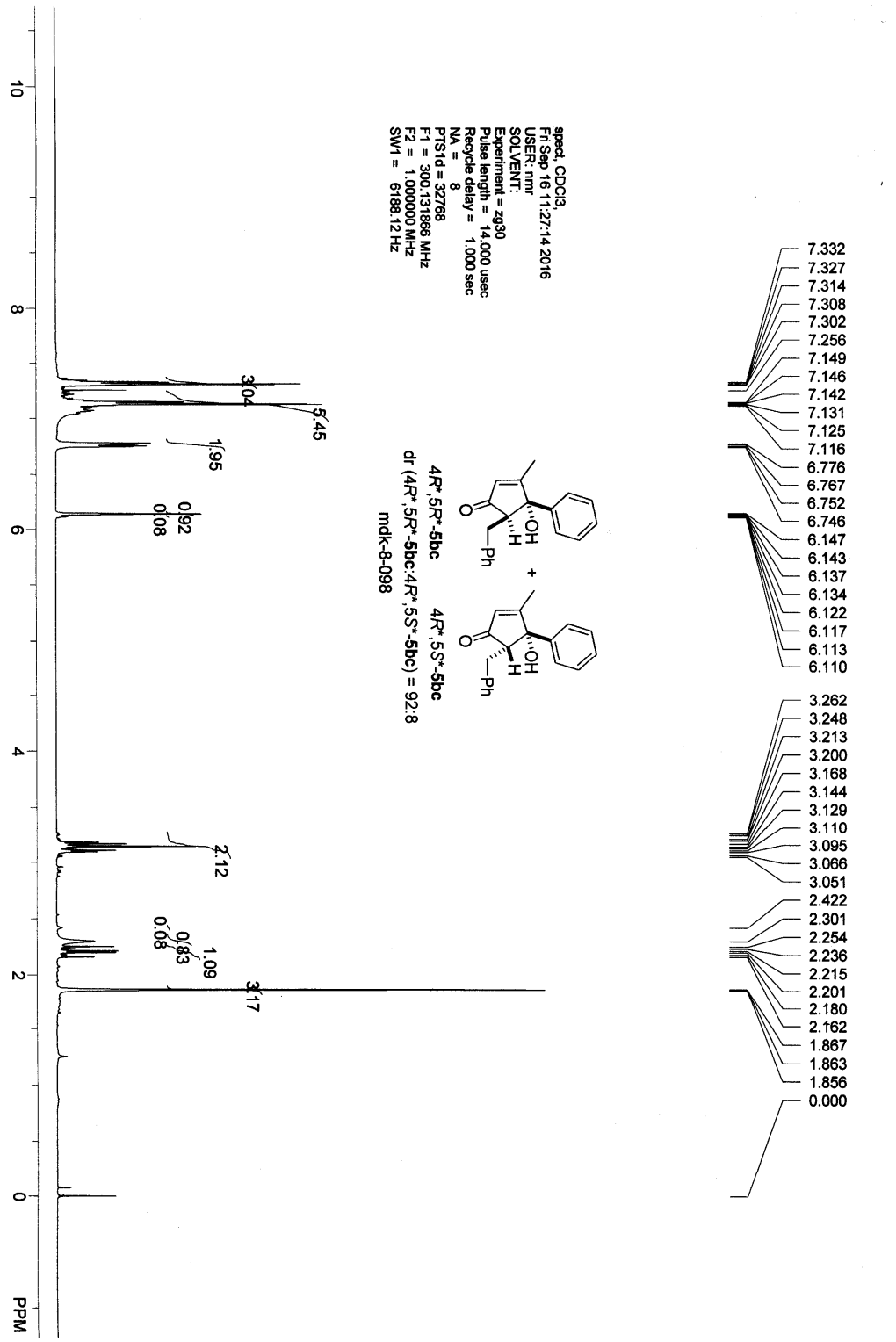

206.110
176.096
138.435
131.323
130.130
127.470
121.627
85.201
77.424
77.000
76.576
61.382
31.602
27.097
25.855
22.132
13.862
13.630
200
150
100
50
0 PPM
spect, CDCl3,
Mon Jan 18 11:32:40 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 1494
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
4R*,5R*-5aa
4R*,5S*-5aa
dr (4R*,5R*-5aa:4R*,5S*-5aa) > 99:1
mdk-9-019-2

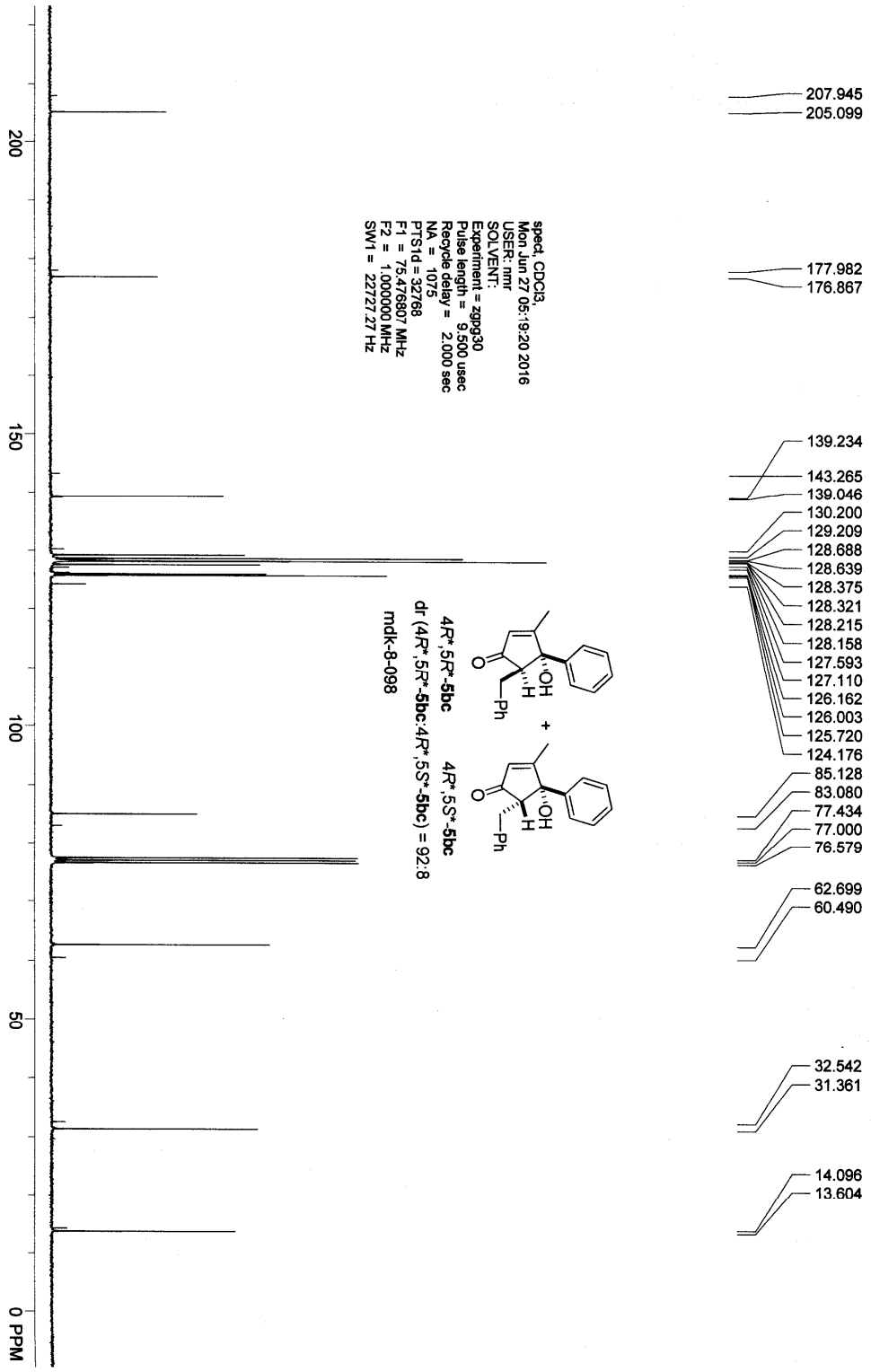

spect, CDCl3,
Fri Sep 16 13:20:15 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131886 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
4R*,5R*-5ba
+
4R*,5S*-5ba
dr (4R*,5R*-5ba:4R*,5S*-5ba) = 99:1
mdk-8-065
7.370
7.346
7.323
7.311
7.305
7.281
7.271
7.263
7.259
7.253
6.147
6.142
6.138
6.134
6.092
6.089
2.813
2.628
2.611
2.598
2.580
1.911
1.906
1.833
1.578
1.560
1.543
1.525
1.515
1.497
1.478
1.460
1.362
1.319
1.284
1.273
1.236
1.219
1.200
1.184
1.141
1.137
1.116
1.108
1.094
1.084
1.076
1.056
1.038
0.986
0.956
0.894
0.848
0.813
0.768
0.746
0.723
0.000
5.01
0.99
1.01
0.97
1.01
3.02
1.02
1.08
6.24
3.04
10
8
6
4
2
0
-2
PPM

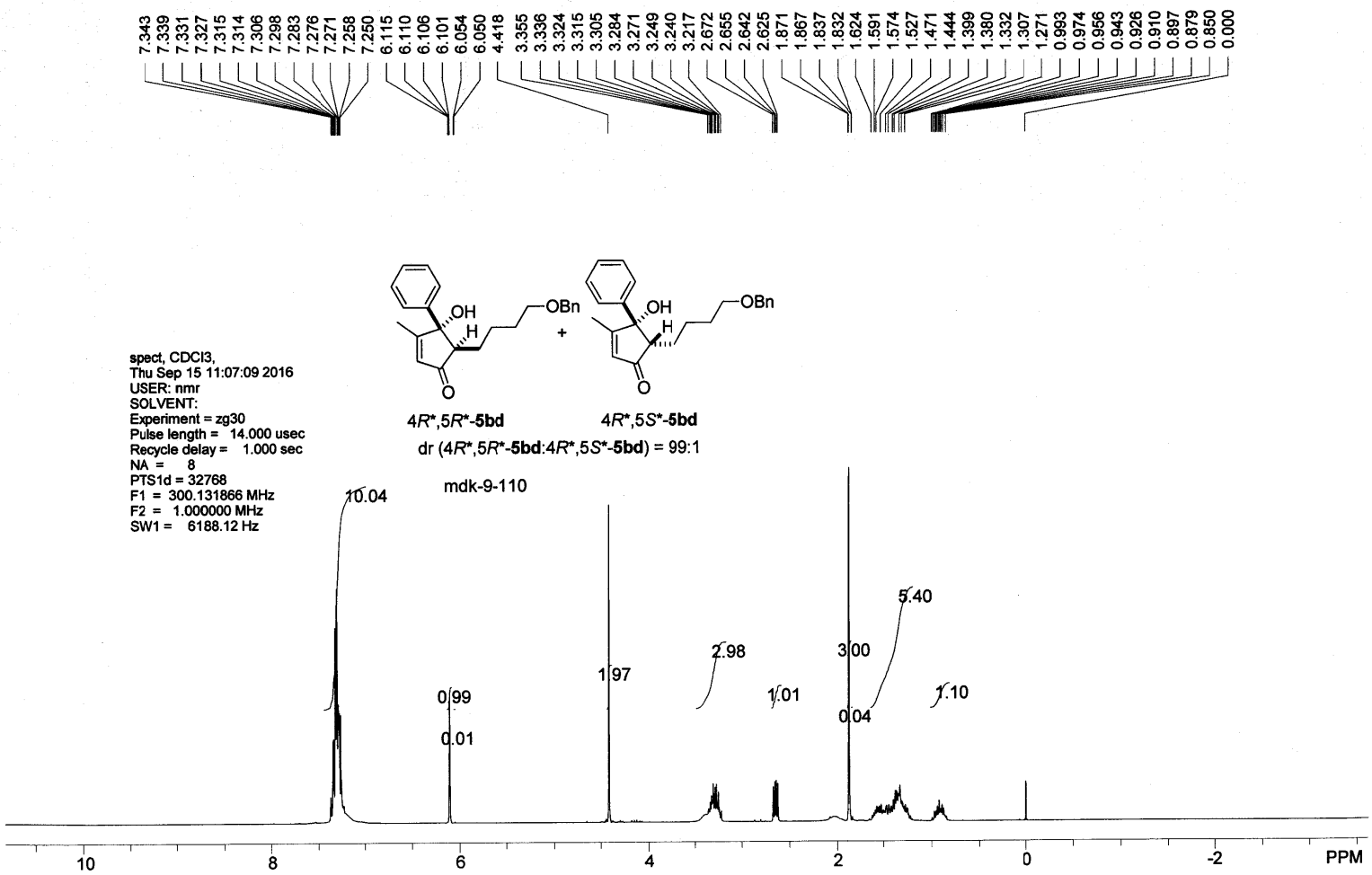

spect, CDCl3
Fri Oct 23 00:49:16 2015
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 561
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
4R*,5R*-5ba
4R*,5S*-5ba
dr (4R*,5R*-5ba:4R*,5S*-5ba) = 99:1
mdk-8-065
206.318
176.126
139.228
130.061
128.242
127.539
125.528
85.569
77.424
77.000
76.576
61.449
31.661
29.667
27.115
25.837
22.092
13.883
13.682
200
150
100
50
0 PPM

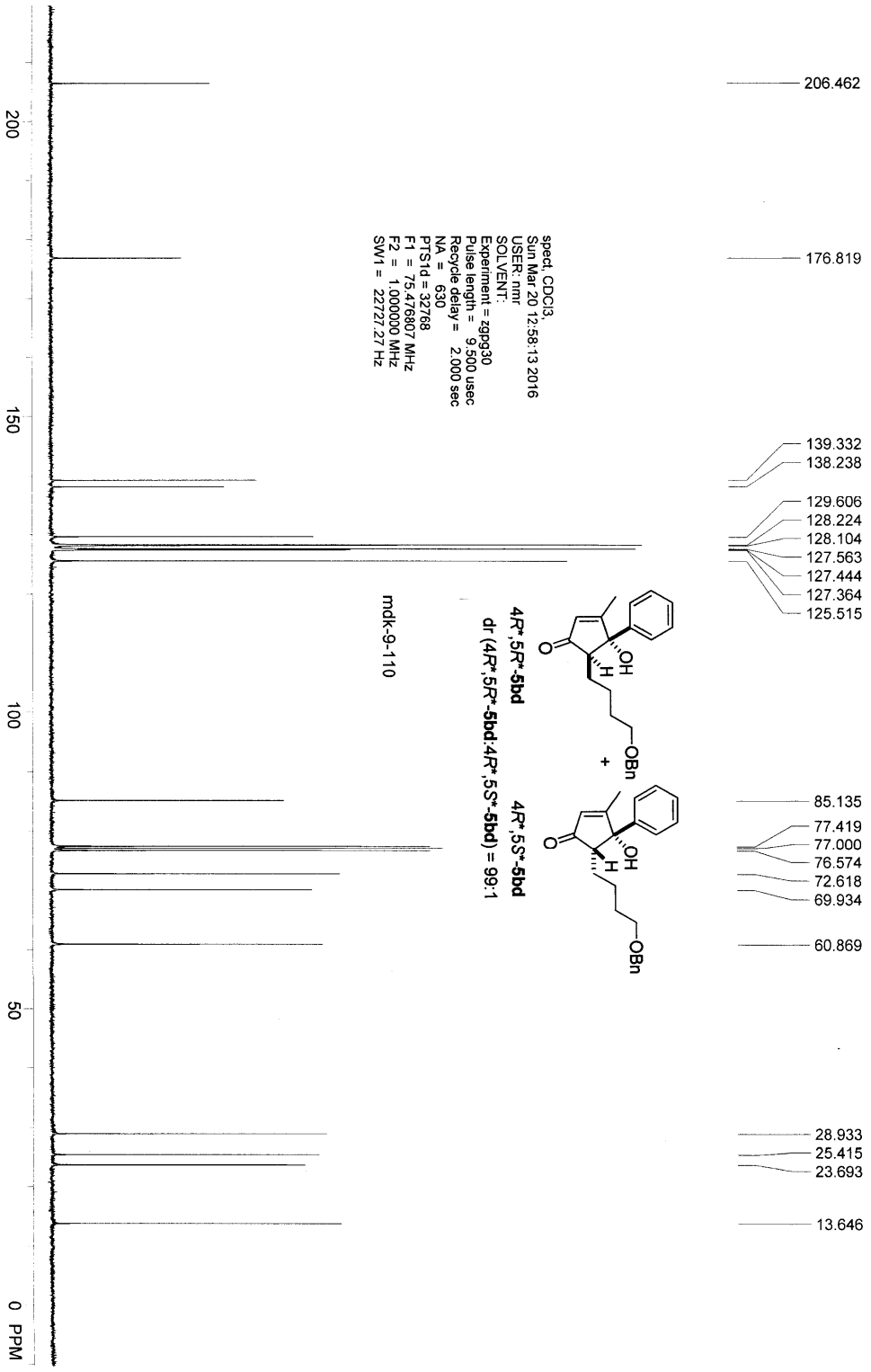

spect, CDCl3,
Thu Oct 29 12:40:40 2015
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 16
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-8-080
4R*,5R*-5bb
4R*,5S*-5bb
dr (4R*,5R*-5bb:4R*,5S*-5bb) = 99:1
5.03
1.00
0.01
0.96
1.02
3.02
1.14
2.27
1.11
3.06
7.344
7.322
7.309
7.303
7.279
7.276
6.141
6.137
6.132
6.127
6.068
6.064
2.667
2.649
2.638
2.620
1.916
1.911
1.533
3.178
1.514
1.498
1.480
1.470
1.453
1.434
1.417
1.397
1.361
1.336
1.304
1.256
1.231
1.215
1.171
0.884
0.868
0.855
0.851
0.839
0.822
0.805
0.793
0.777
0.761
0.717
0.692
0.668
0.000
10
8
6
4
2
0
-2
PPM

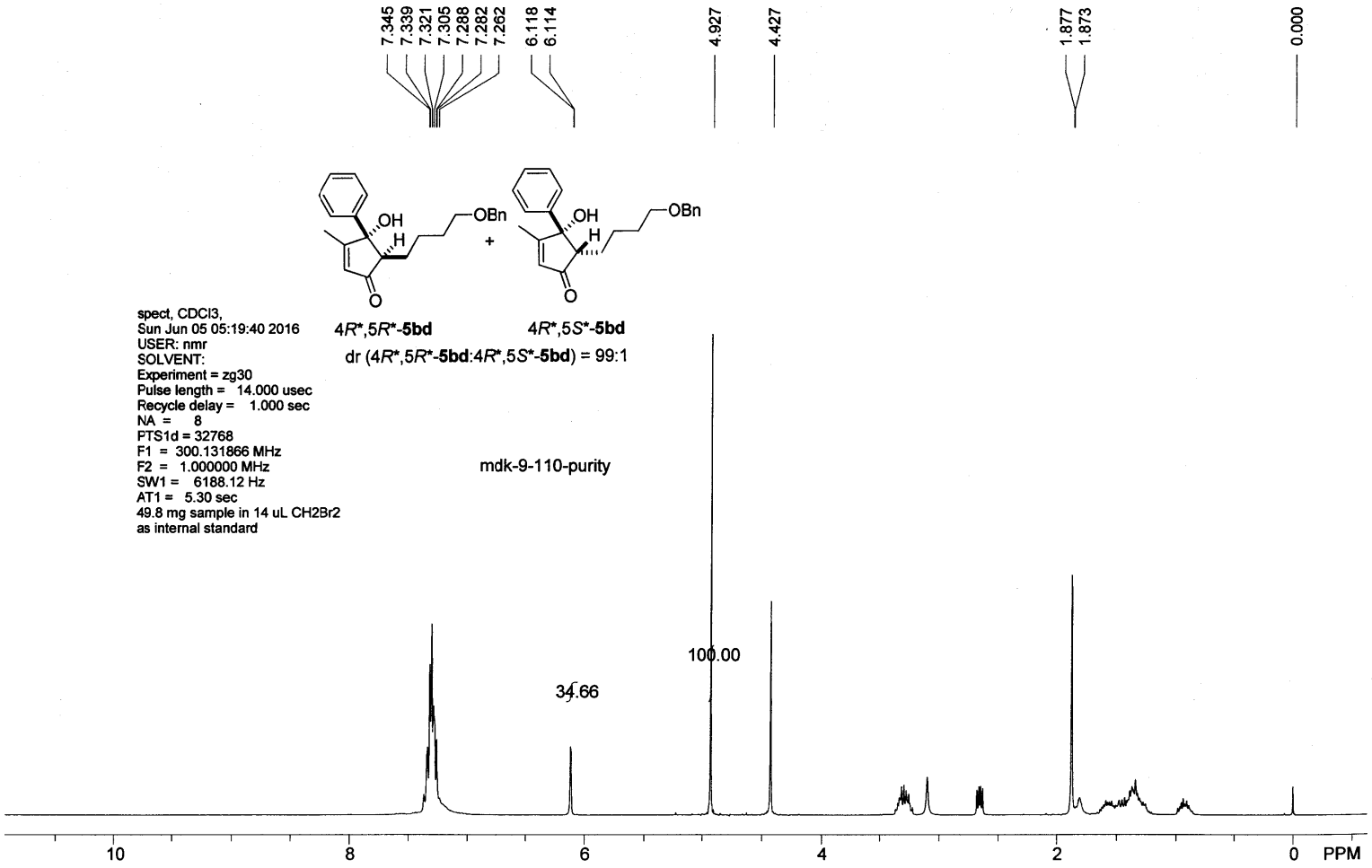

206.676
176.573
139.277
129.909
128.201
127.474
125.504
85.465
77.425
77.000
76.576
61.133
28.063
20.782
13.934
13.705
250
200
150
100
50
0
PPM
spect, CDCl3,
Thu Oct 29 14:37:04 2015
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 10005
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-8-080
4R*,5R*-5bb
4R*,5S*-5bb
dr (4R*,5R*-5bb:4R*,5S*-5bb) = 99:1

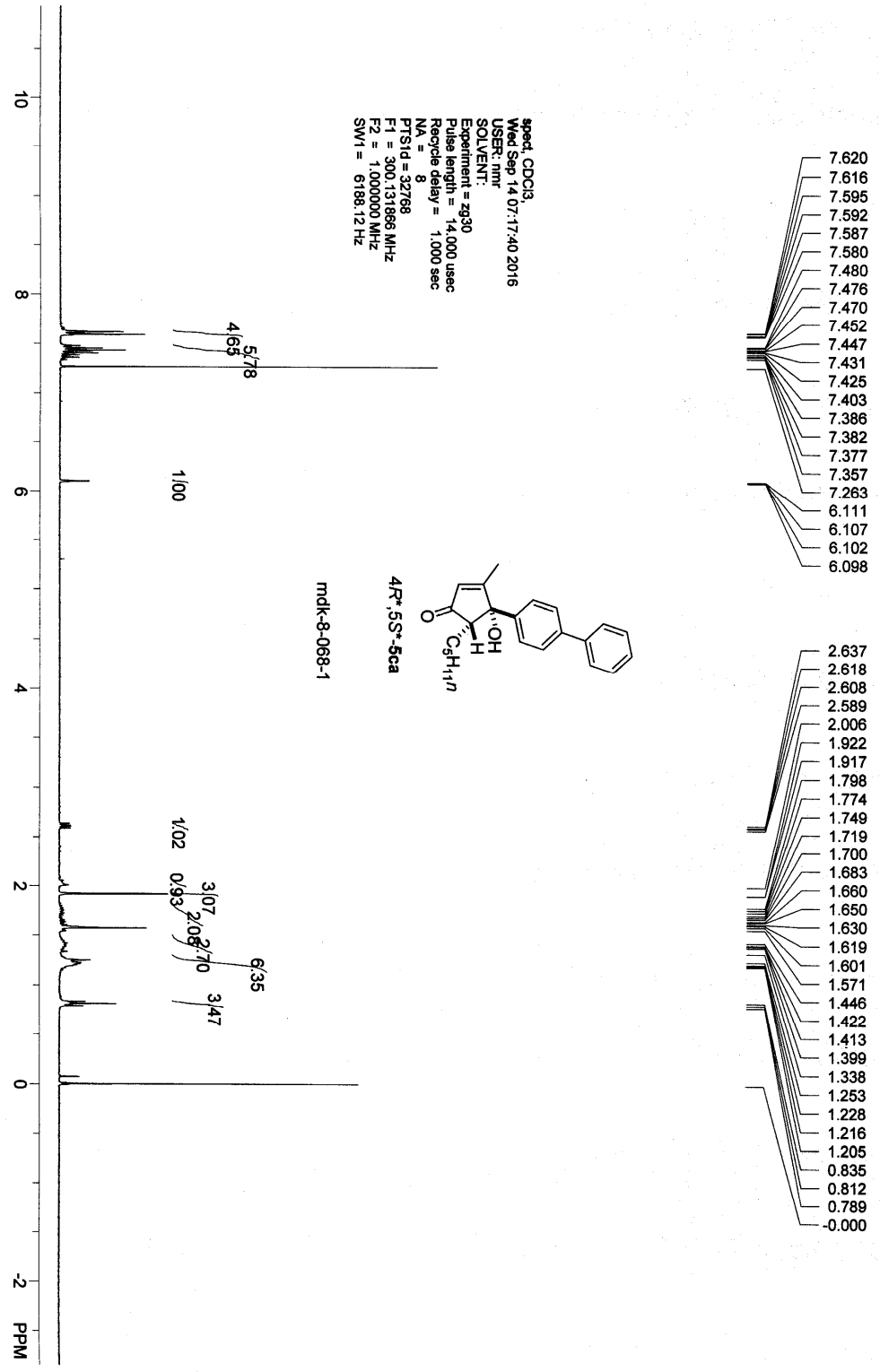

spect. CDCl3
Fri Sep 16 11:27:14 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
4R*,5R*-5bc
4R*,5S*-5bc
dr (4R*,5R*-5bc:4R*,5S*-5bc) = 92:8
mdk-8-098
OH
H
Ph
O
3.04
5.45
1.95
0.92
0.08
2.12
0.83
0.08
1.09
3.17
10
8
6
4
2
0
PPM
7.332
7.327
7.314
7.308
7.302
7.256
7.149
7.146
7.142
7.131
7.125
7.116
6.776
6.767
6.752
6.746
6.147
6.143
6.137
6.134
6.122
6.117
6.113
6.110
3.262
3.248
3.213
3.200
3.168
3.144
3.129
3.110
3.095
3.066
3.051
2.422
2.301
2.254
2.236
2.215
2.201
2.180
2.162
1.867
1.863
1.856
0.000

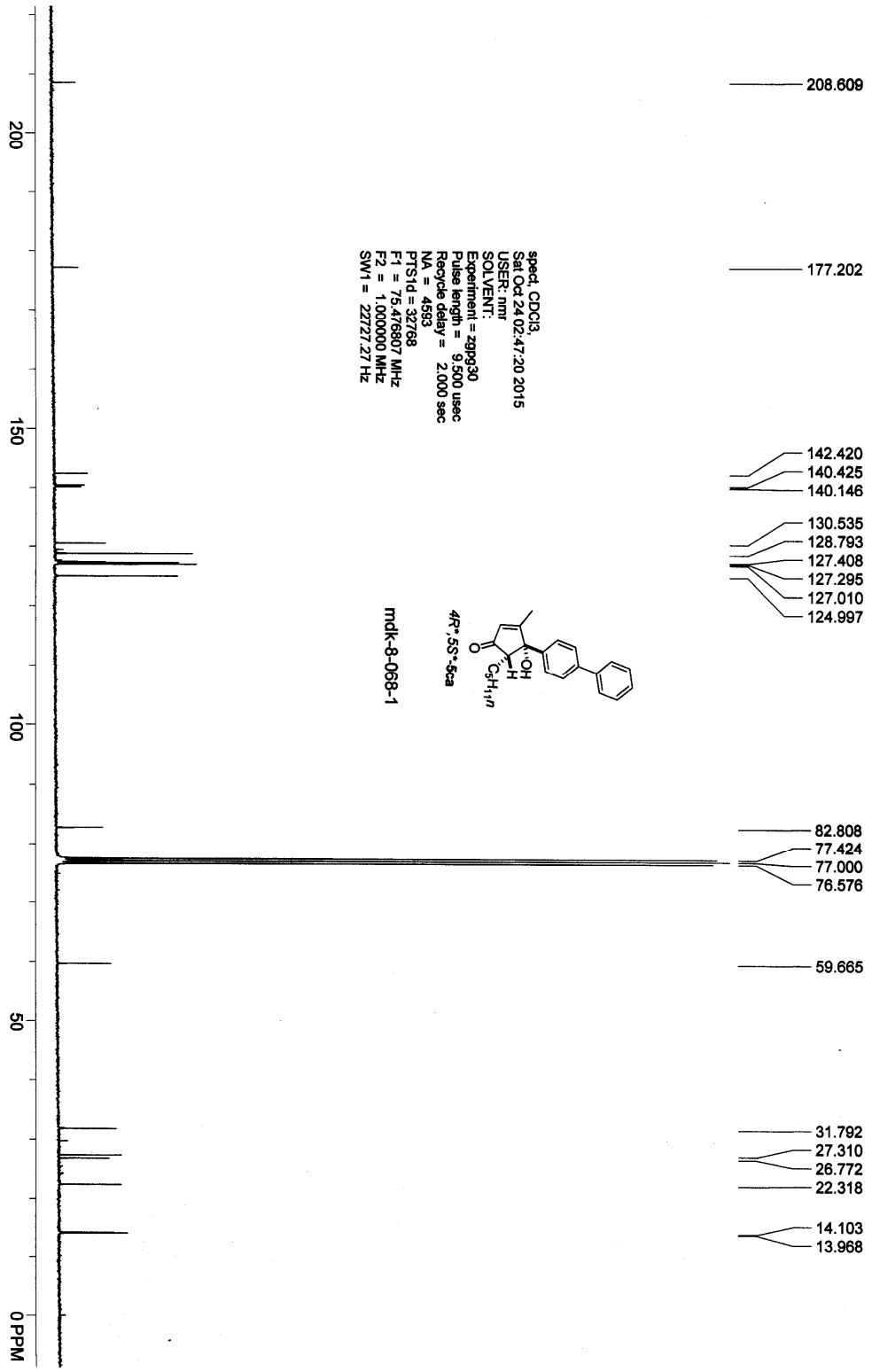

207.945
205.099
177.982
176.867
139.234
143.265
139.046
130.200
129.209
128.688
128.639
128.375
128.321
128.215
128.158
127.593
127.110
126.162
126.003
125.720
124.176
85.128
83.080
77.434
77.000
76.579
62.699
60.490
32.542
31.361
14.096
13.604
200
150
100
50
0 PPM
spect, CDCl3,
Mon Jun 27 05:19:20 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 1075
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
OH
H
Ph
+
OH
H
Ph
4R*,5R*-5bc
4R*,5S*-5bc
dr (4R*,5R*-5bc:4R*,5S*-5bc) = 92:8
mdk-8-098

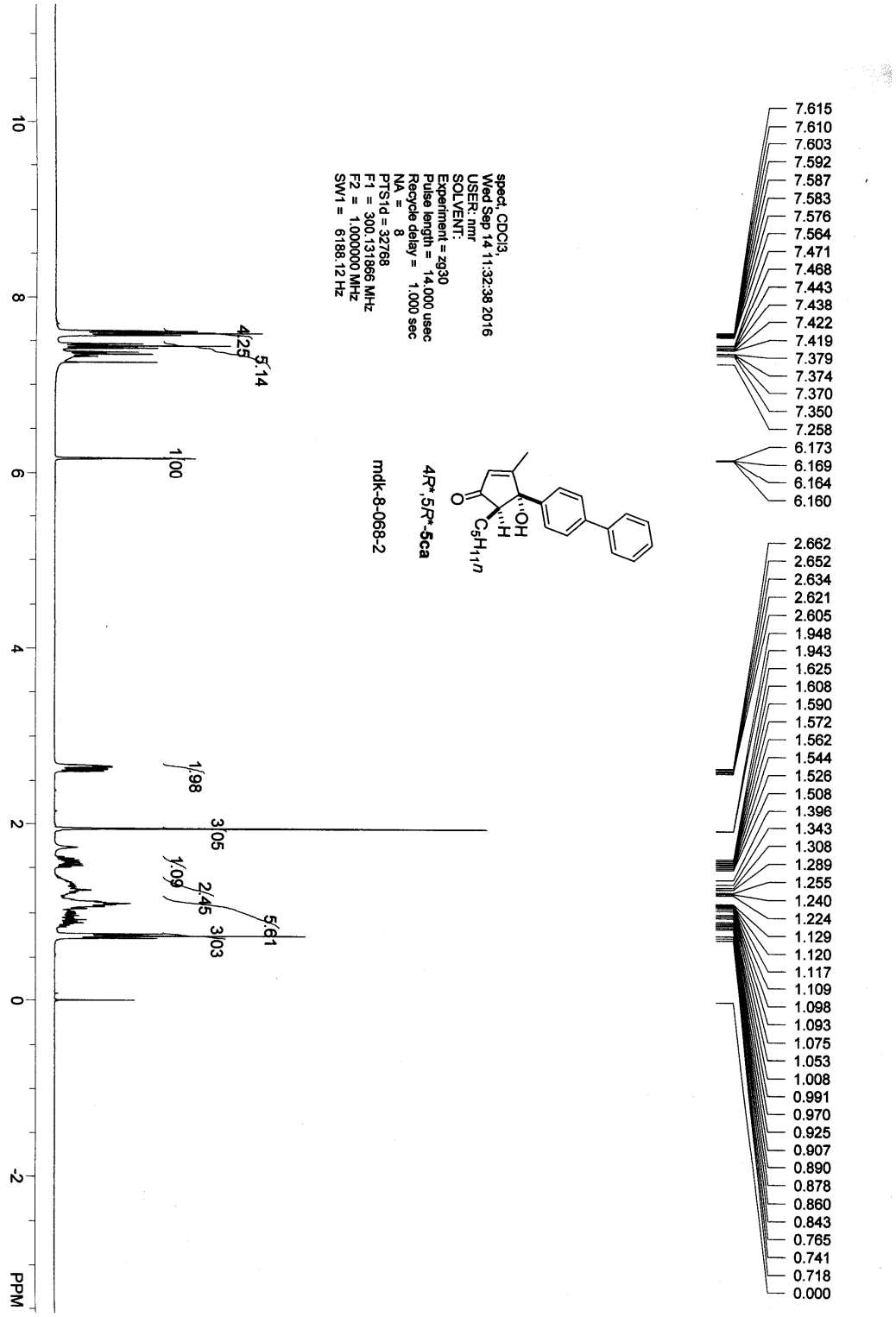

7.343
7.339
7.331
7.327
7.315
7.314
7.306
7.298
7.283
7.276
7.271
7.258
7.250
6.115
6.110
6.106
6.101
6.054
6.050
4.418
3.355
3.336
3.324
3.315
3.305
3.284
3.271
3.249
3.240
3.217
2.672
2.655
2.642
2.625
1.871
1.867
1.837
1.832
1.624
1.591
1.574
1.527
1.471
1.444
1.399
1.380
1.332
1.307
1.271
0.993
0.974
0.956
0.943
0.926
0.910
0.897
0.879
0.850
0.000
OH
H
OBn
+
O
4R*,5R*-5bd
4R*,5S*-5bd
dr (4R*,5R*-5bd:4R*,5S*-5bd) = 99:1
spect, CDCl3,
Thu Sep 15 11:07:09 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-9-110
10.04
0.99
0.01
1.97
2.98
1.01
3.00
0.04
5.40
1.10
10
8
6
4
2
0
-2
PPM

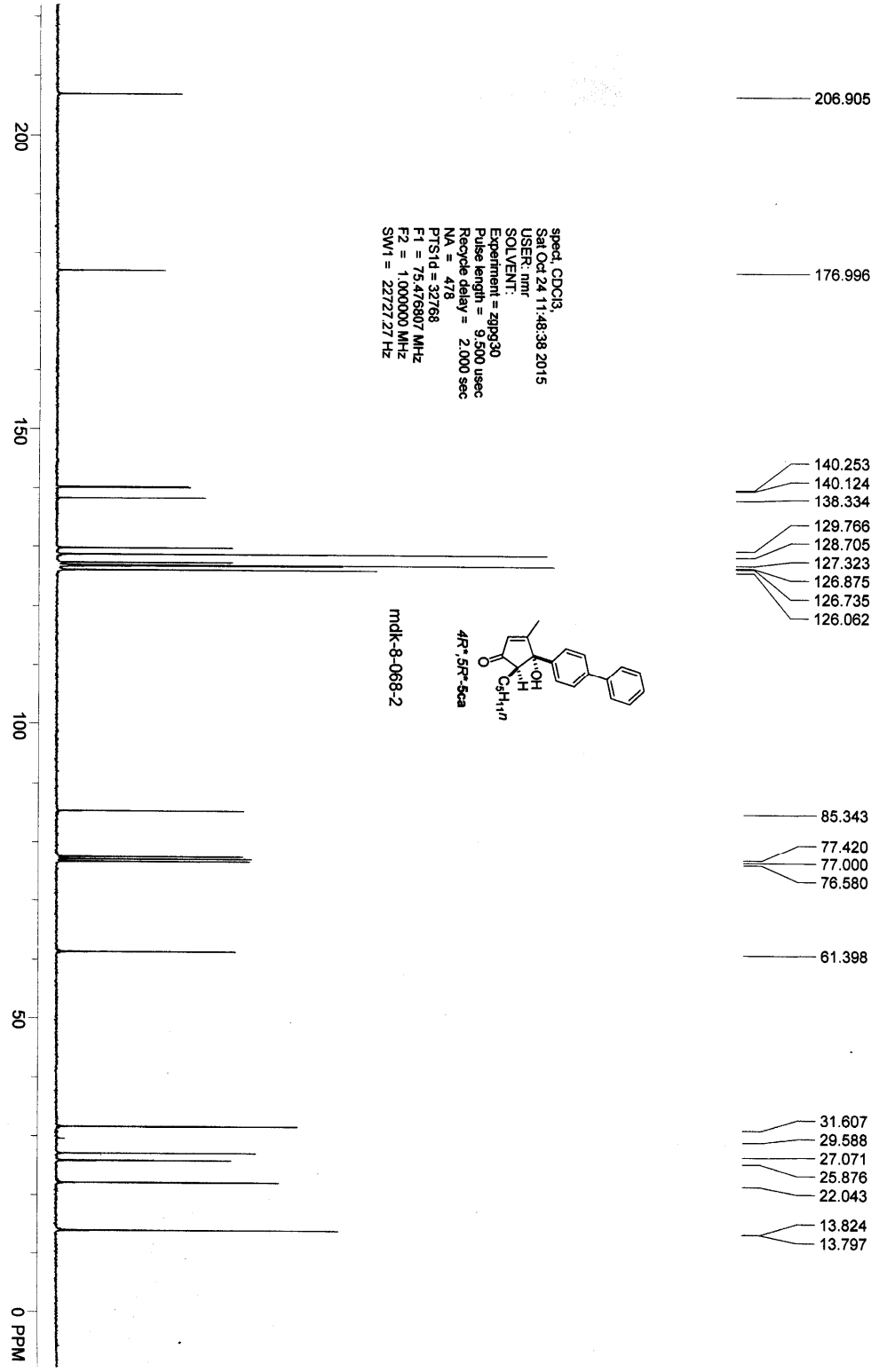

206.462
176.819
139.332
138.238
129.606
128.224
128.104
127.563
127.444
127.364
125.515
85.135
77.419
77.000
76.574
72.618
69.934
60.869
28.933
25.415
23.693
13.646
200
150
100
50
0 PPM
spect_CDCl3
Sun Mar 20 12:58:13 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 630
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-9-110
4R*,5R*-5bd
dr (4R*,5R*-5bd:4R*,5S*-5bd) = 99:1
4R*,5S*-5bd
OH
H
O
OBn
+

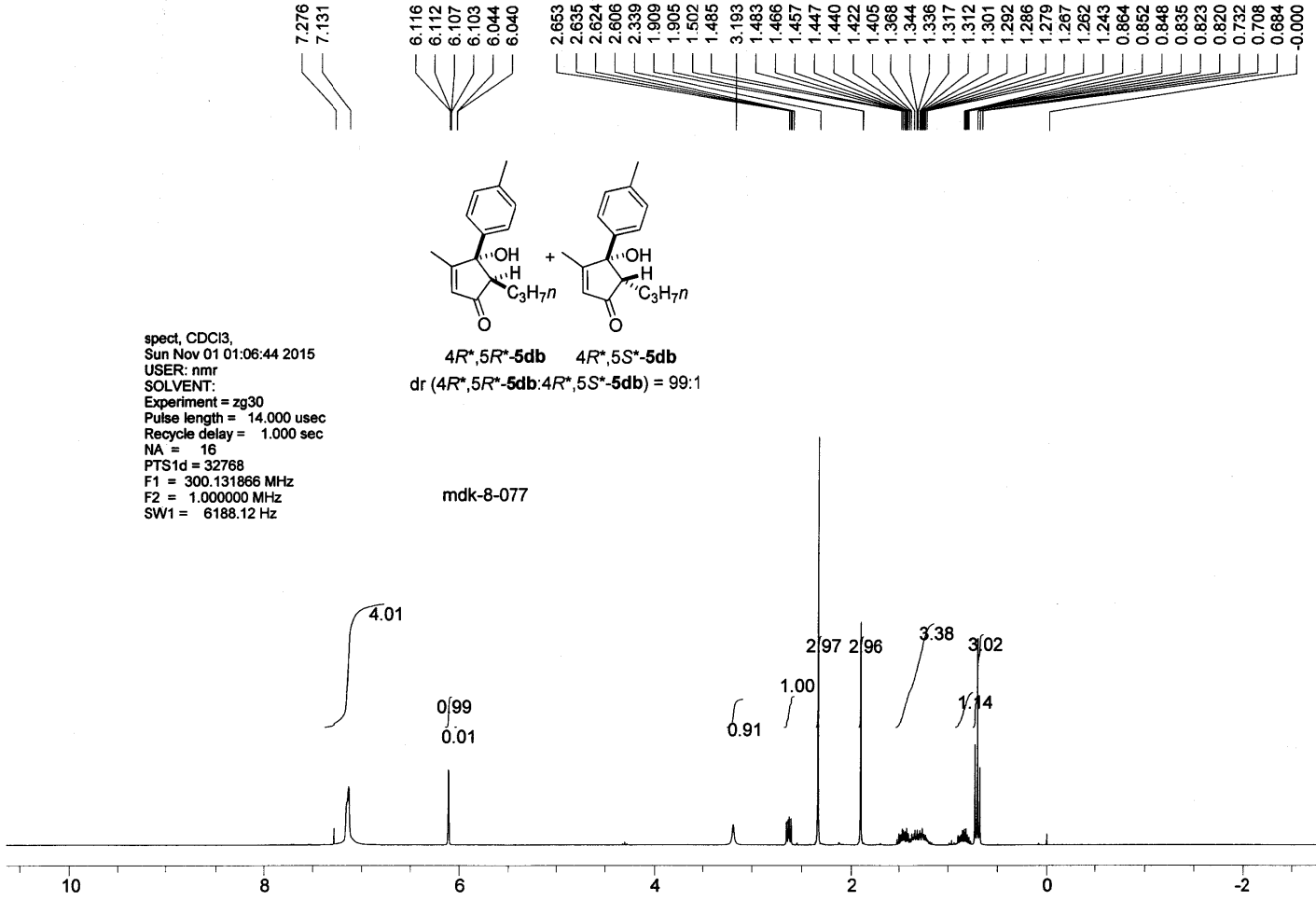

7.345
7.339
7.321
7.305
7.288
7.282
7.262
6.118
6.114
4.927
4.427
1.877
1.873
0.000
OH
H
OBn
+
OH
H
OBn
O
O
spect, CDCl3,
Sun Jun 05 05:19:40 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
AT1 = 5.30 sec
49.8 mg sample in 14 uL CH2Br2
as internal standard
4R*,5R*-5bd
4R*,5S*-5bd
dr (4R*,5R*-5bd:4R*,5S*-5bd) = 99:1
mdk-9-110-purity
34.66
100.00
10
8
6
4
2
0
PPM

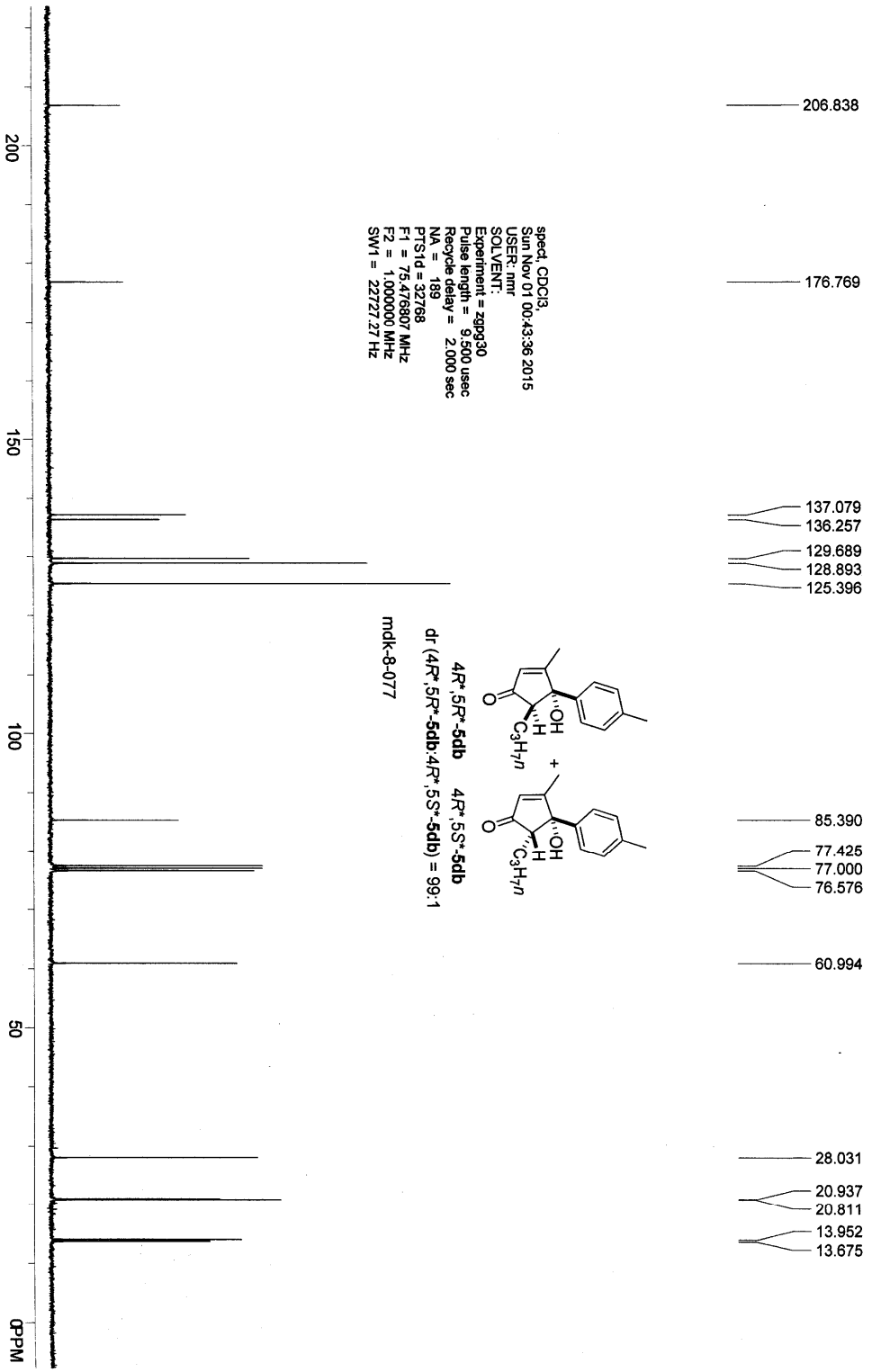

spect, CDCl3,
Wed Sep 14 07:17:40 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.1318 66 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
4.65
5.78
1.00
1.02
0.93
3.07
2.08
2.70
6.35
3.47
mdk-8-068-1
4R*,5S*-5ca
OH
H
C5H11n
O
7.620
7.616
7.595
7.592
7.587
7.580
7.480
7.476
7.470
7.452
7.447
7.431
7.425
7.403
7.386
7.382
7.377
7.357
7.263
6.111
6.107
6.102
6.098
2.637
2.618
2.608
2.589
2.006
1.922
1.917
1.798
1.774
1.749
1.719
1.700
1.683
1.660
1.650
1.630
1.619
1.601
1.571
1.446
1.422
1.413
1.399
1.338
1.253
1.228
1.216
1.205
0.835
0.812
0.789
-0.000
10
8
6
4
2
0
-2
PPM

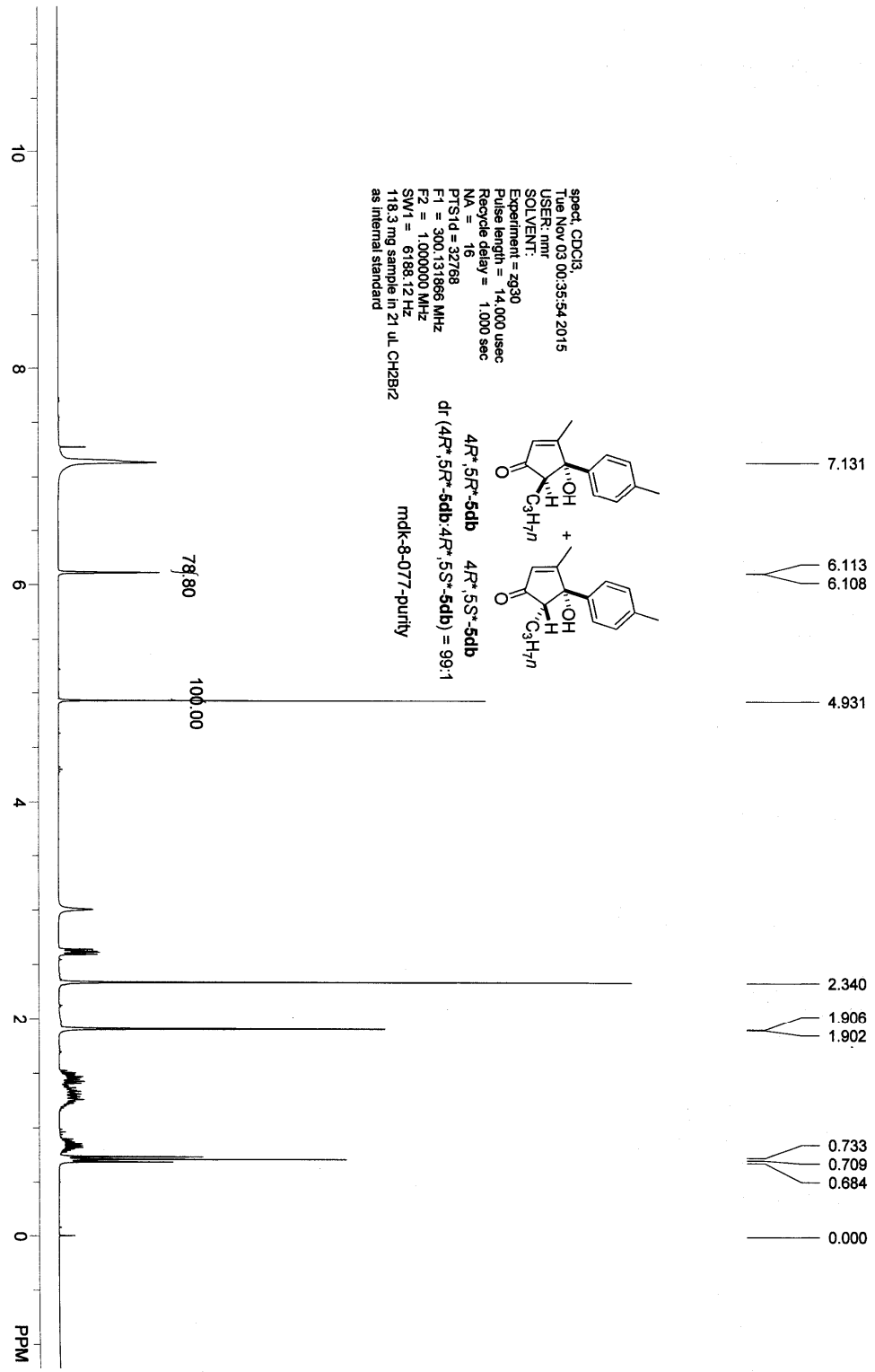

208.609
177.202
142.420
140.425
140.146
130.535
128.793
127.408
127.295
127.010
124.997
82.808
77.424
77.000
76.576
59.665
31.792
27.310
26.772
22.318
14.103
13.968
200
150
100
50
0 PPM
spect, CDCl3,
Sat Oct 24 02:47:20 2015
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 4593
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-8-068-1
4R*,5S*-5ca
OH
H
O
C5H11n

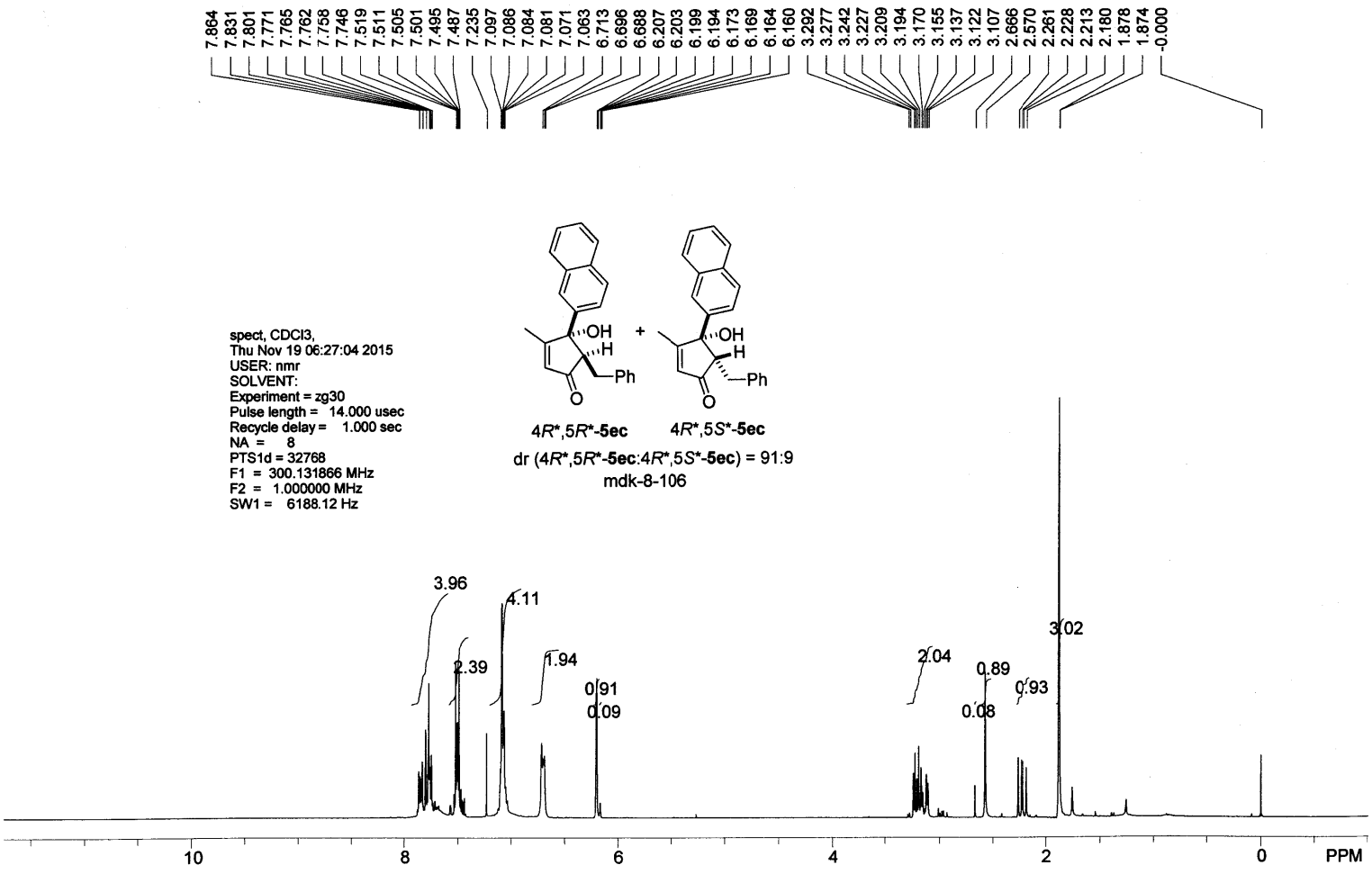

spect. CDCl3
Wed Sep 14 11:32:38 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-8-068-2
4R*,5R*-5ca
OH
H
C5H11-n
O
7.615
7.610
7.603
7.592
7.587
7.583
7.576
7.564
7.471
7.468
7.443
7.438
7.422
7.419
7.379
7.374
7.370
7.350
7.258
6.173
6.169
6.164
6.160
2.662
2.652
2.634
2.621
2.605
1.948
1.943
1.625
1.608
1.590
1.572
1.562
1.544
1.526
1.508
1.396
1.343
1.308
1.289
1.255
1.240
1.224
1.129
1.120
1.117
1.109
1.098
1.093
1.075
1.053
1.008
0.991
0.970
0.925
0.907
0.890
0.878
0.860
0.843
0.765
0.741
0.718
0.000
4.25
5.14
1.00
1.98
3.05
1.09
2.45
3.03
5.61
10
8
6
4
2
0
-2
PPM

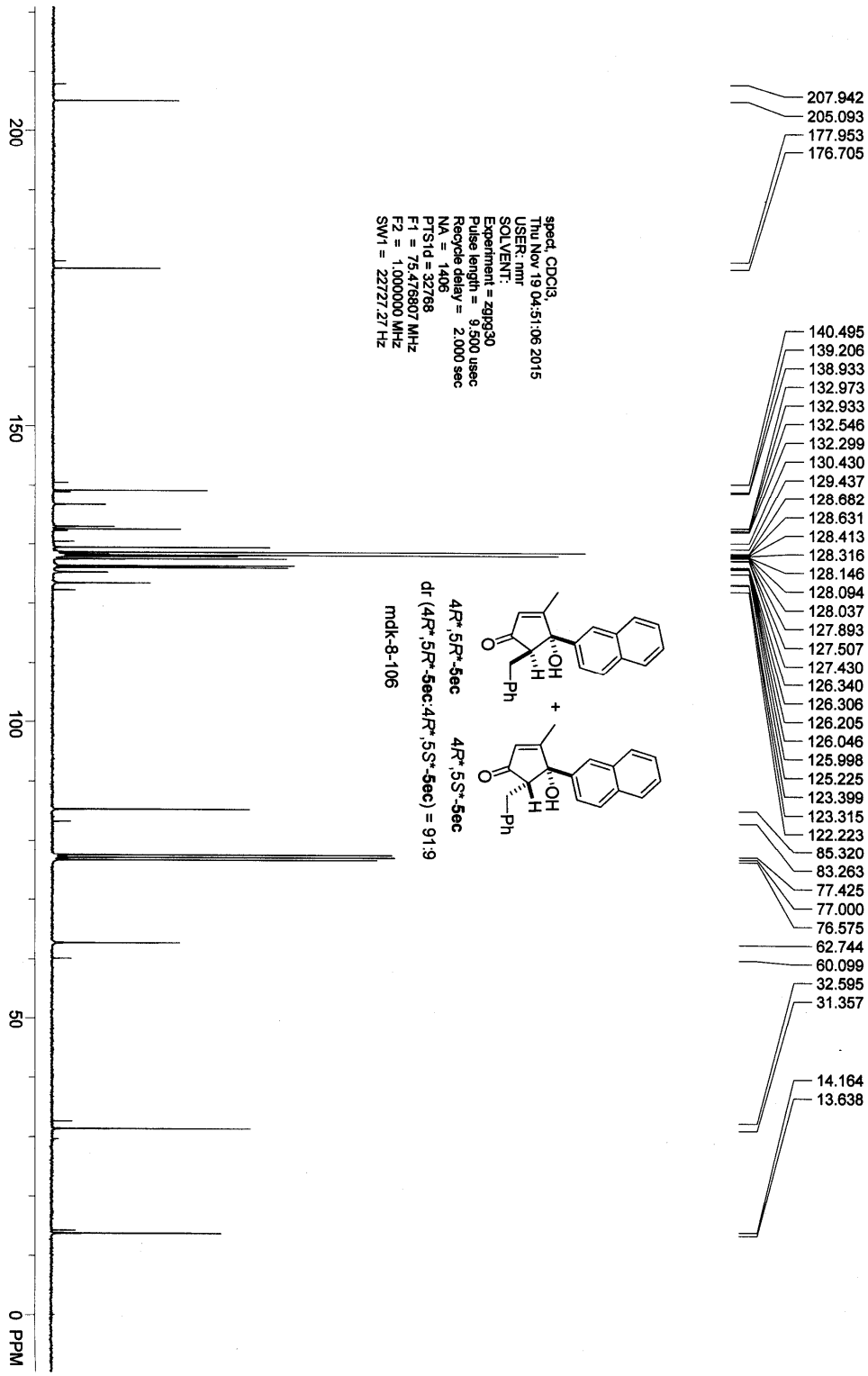

206.905
176.996
140.253
140.124
138.334
129.766
128.705
127.323
126.875
126.735
126.062
85.343
77.420
77.000
76.580
61.398
31.607
29.588
27.071
25.876
22.043
13.824
13.797
200
150
100
50
0 PPM
spect, CDCl3,
Sat Oct 24 11:48:38 2015
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 478
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-8-068-2
4R*,5R*-5ca
OH
H
C5H11n
O

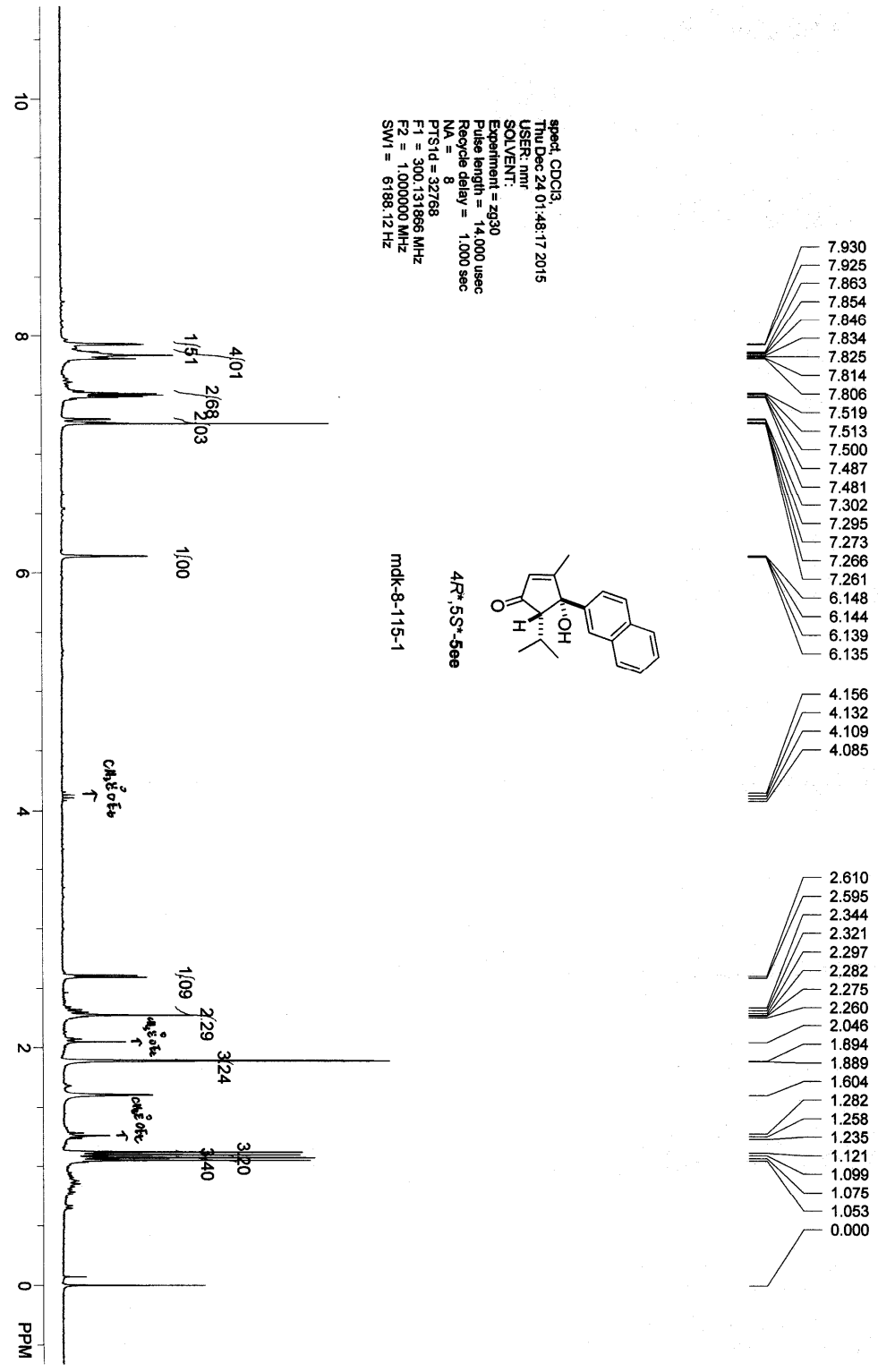

7.276
7.131
6.116
6.112
6.107
6.103
6.044
6.040
2.653
2.635
2.624
2.606
2.339
1.909
1.905
1.502
1.485
3.193
1.483
1.466
1.457
1.447
1.440
1.422
1.405
1.368
1.344
1.336
1.317
1.312
1.301
1.292
1.286
1.279
1.267
1.262
1.243
0.864
0.852
0.848
0.835
0.823
0.820
0.732
0.708
0.684
-0.000
OH
H
C3H7n
+
OH
H
C3H7n
4R*,5R*-5db
4R*,5S*-5db
dr (4R*,5R*-5db:4R*,5S*-5db) = 99:1
spect, CDCl3,
Sun Nov 01 01:06:44 2015
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 16
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-8-077
4.01
0.99
0.01
0.91
1.00
2.97
2.96
3.38
3.02
1.14
10
8
6
4
2
0
-2
PPM

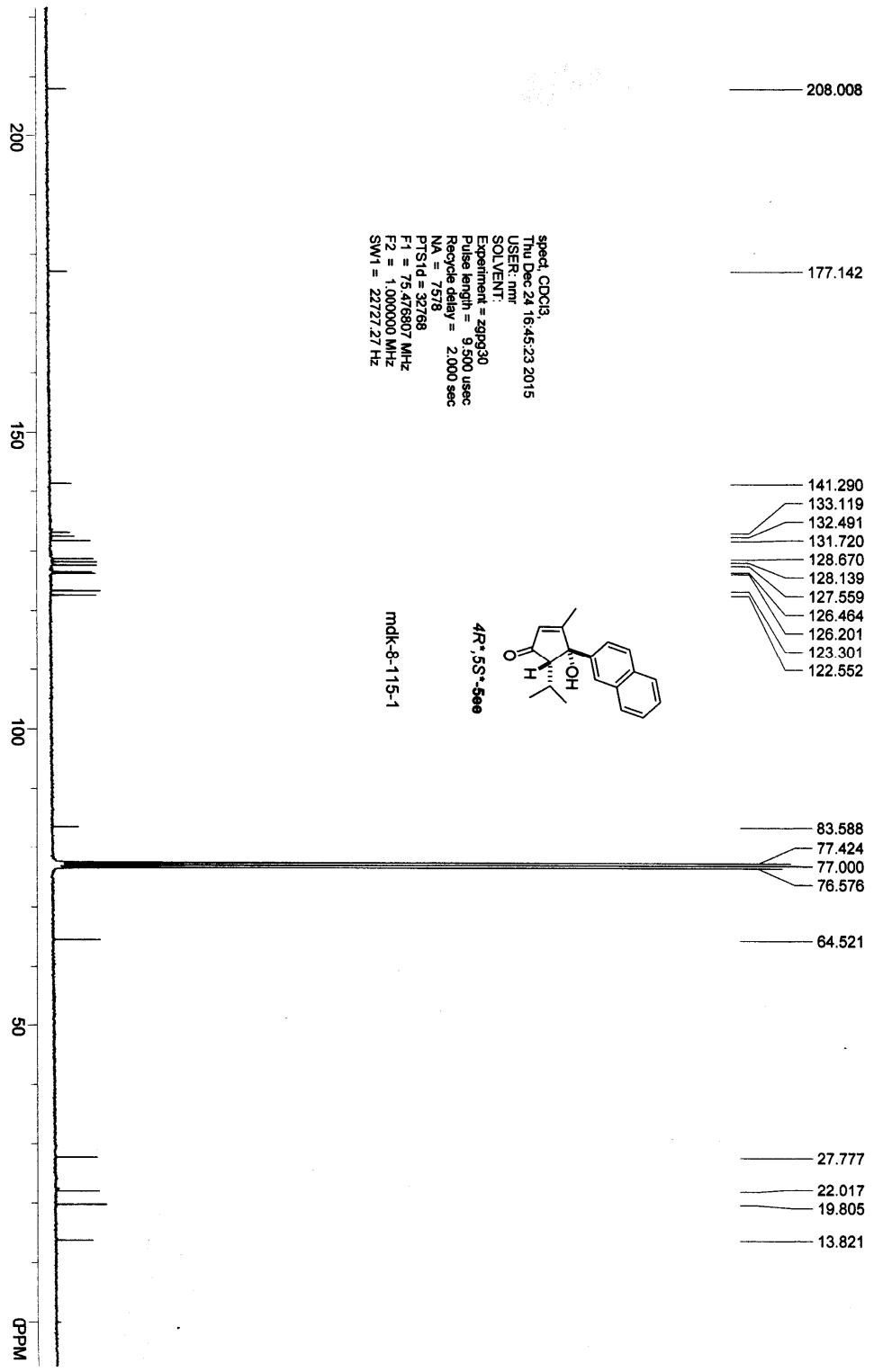

206.838
176.769
137.079
136.257
129.689
128.893
125.396
85.390
77.425
77.000
76.576
60.994
28.031
20.937
20.811
13.952
13.675
200
150
100
50
0PPM
spect, CDCl3,
Sun Nov 01 00:43:36 2015
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 189
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-8-077
dr (4R*,5R*-5db:4R*,5S*-5db) = 99:1
4R*,5R*-5db
4R*,5S*-5db
OH
H
C3H7-n
O
+

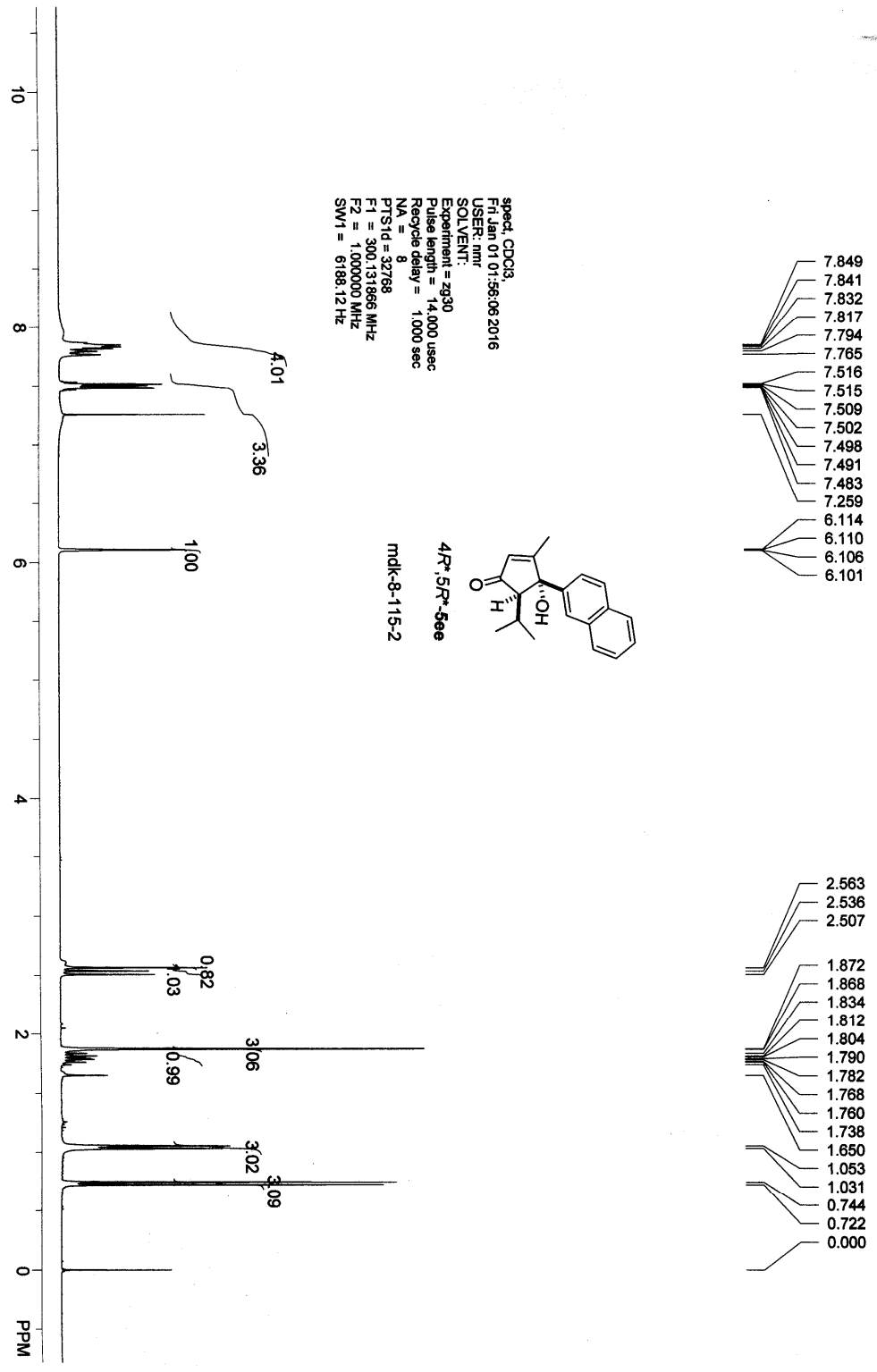

spect, CDCl3,
Tue Nov 03 00:35:54 2015
USER: mnr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 16
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
118.3 mg sample in 21 uL CH2Br2
as internal standard
mdk-8-077-purity
dr (4R*,5R*-5db:4R*,5S*-5db) = 99:1
4R*,5R*-5db
4R*,5S*-5db
OH
H
C3H7-n
+
7.131
6.113
6.108
4.931
2.340
1.906
1.902
0.733
0.709
0.684
0.000
78.80
100.00
10
8
6
4
2
0
PPM

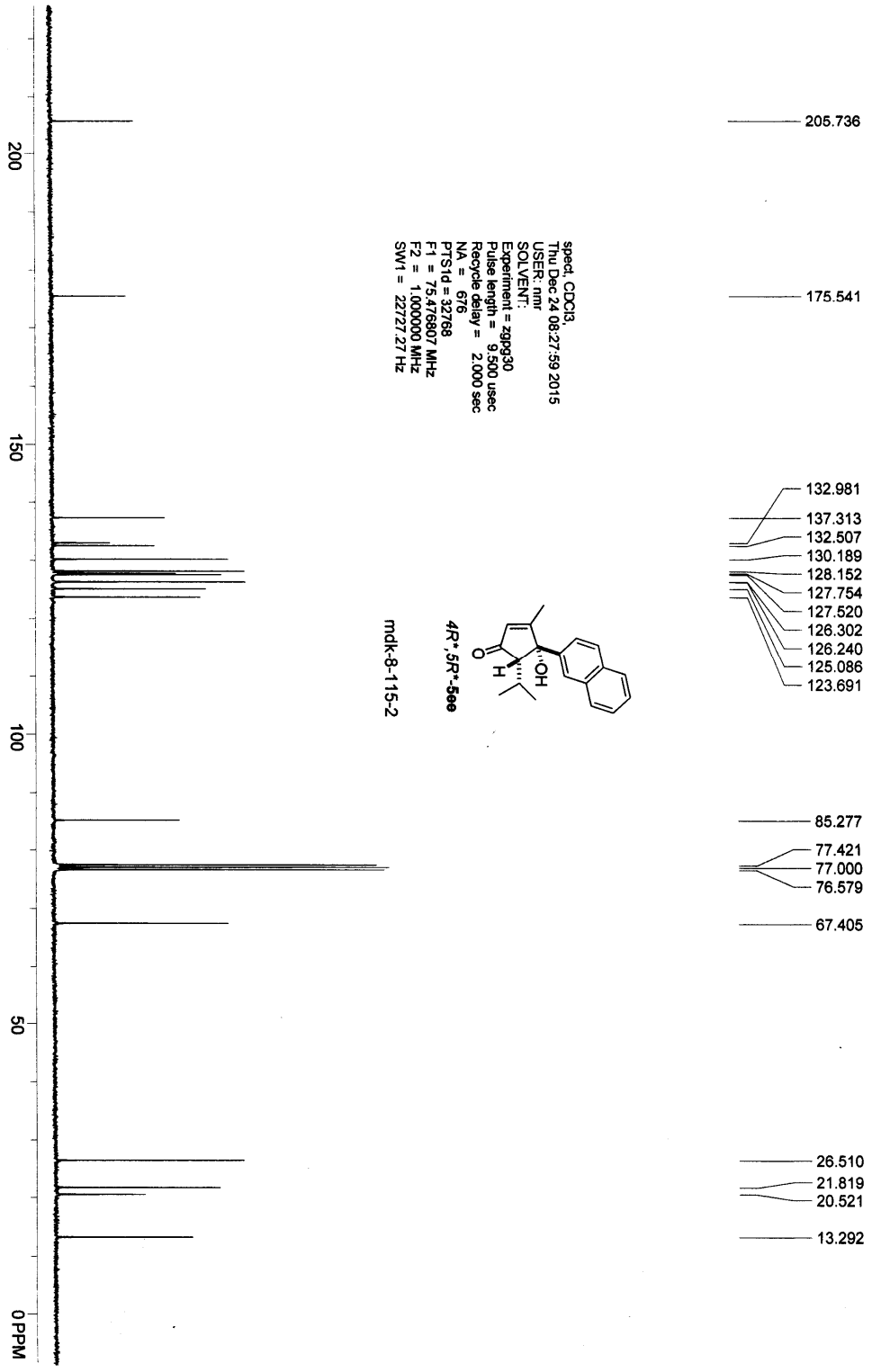

7.864
7.831
7.801
7.771
7.765
7.762
7.758
7.746
7.519
7.511
7.505
7.501
7.495
7.487
7.235
7.097
7.086
7.084
7.081
7.071
7.063
6.713
6.696
6.688
6.207
6.203
6.199
6.194
6.173
6.169
6.164
6.160
3.292
3.277
3.242
3.227
3.209
3.194
3.170
3.155
3.137
3.122
3.107
2.666
2.570
2.261
2.228
2.213
2.180
1.878
1.874
-0.000
spect, CDCl3,
Thu Nov 19 06:27:04 2015
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
OH
H
Ph
O
+
4R*,5R*-5ec
4R*,5S*-5ec
dr (4R*,5R*-5ec:4R*,5S*-5ec) = 91:9
mdk-8-106
3.96
4.11
2.39
1.94
0.91
0.09
2.04
0.89
0.08
0.93
3.02
10
8
6
4
2
0
PPM

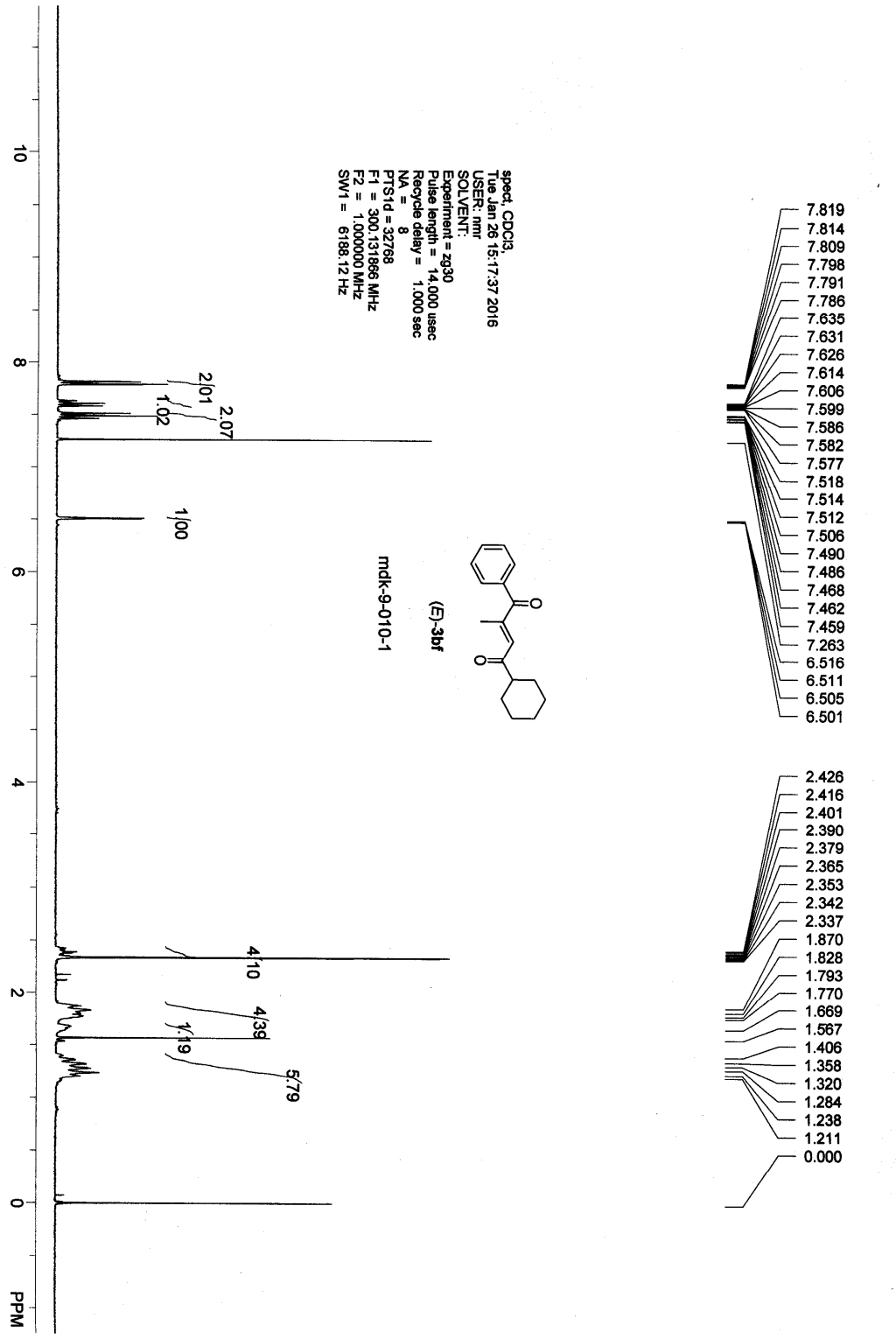

207.942
205.093
177.953
176.705
140.495
139.206
138.933
132.973
132.933
132.546
132.299
130.430
129.437
128.682
128.631
128.413
128.316
128.146
128.094
128.037
127.893
127.507
127.430
126.340
126.306
126.205
126.046
125.998
125.225
123.399
123.315
122.223
85.320
83.263
77.425
77.000
76.575
62.744
60.099
32.595
31.357
14.164
13.638
200
150
100
50
0 PPM
spect, CDCl3,
Thu Nov 19 04:51:06 2015
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 1406
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
OH
H
Ph
O
+
4R*,5R*-5ec
4R*,5S*-5ec
dr (4R*,5R*-5ec:4R*,5S*-5ec) = 91:9
mdk-8-106

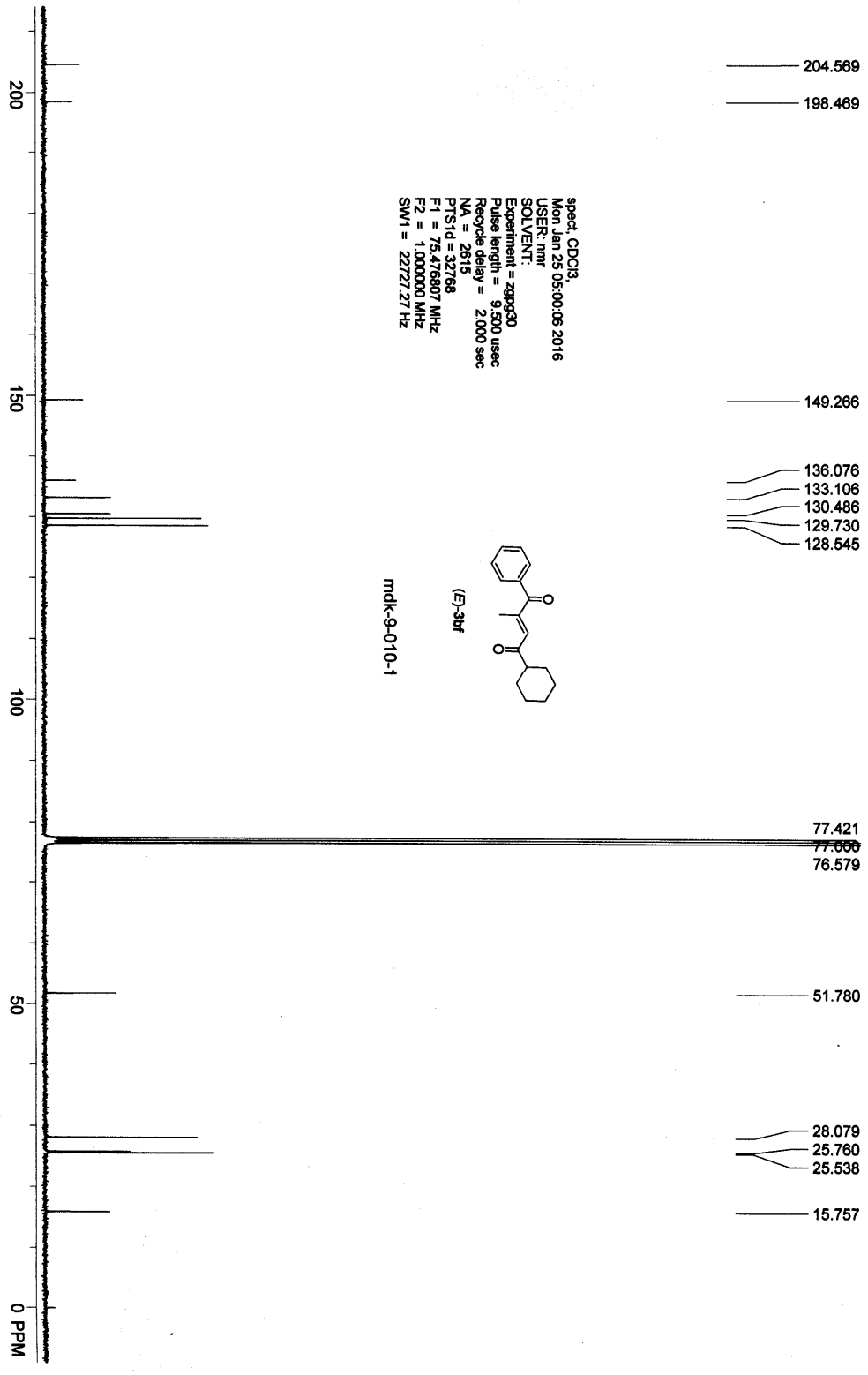

spect_CDCl3
Thu Dec 24 01:48:17 2015
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
4R*,5S*-5ee
mdk-8-115-1
OH
O
H
7.930
7.925
7.863
7.854
7.846
7.834
7.825
7.814
7.806
7.519
7.513
7.500
7.487
7.481
7.302
7.295
7.273
7.266
7.261
6.148
6.144
6.139
6.135
4.156
4.132
4.109
4.085
2.610
2.595
2.344
2.321
2.297
2.282
2.275
2.260
2.046
1.894
1.889
1.604
1.282
1.258
1.235
1.121
1.099
1.075
1.053
0.000
4.01
1.51
2.68
2.03
1.00
1.09
2.29
3.24
3.20
3.40
10
8
6
4
2
0
PPM

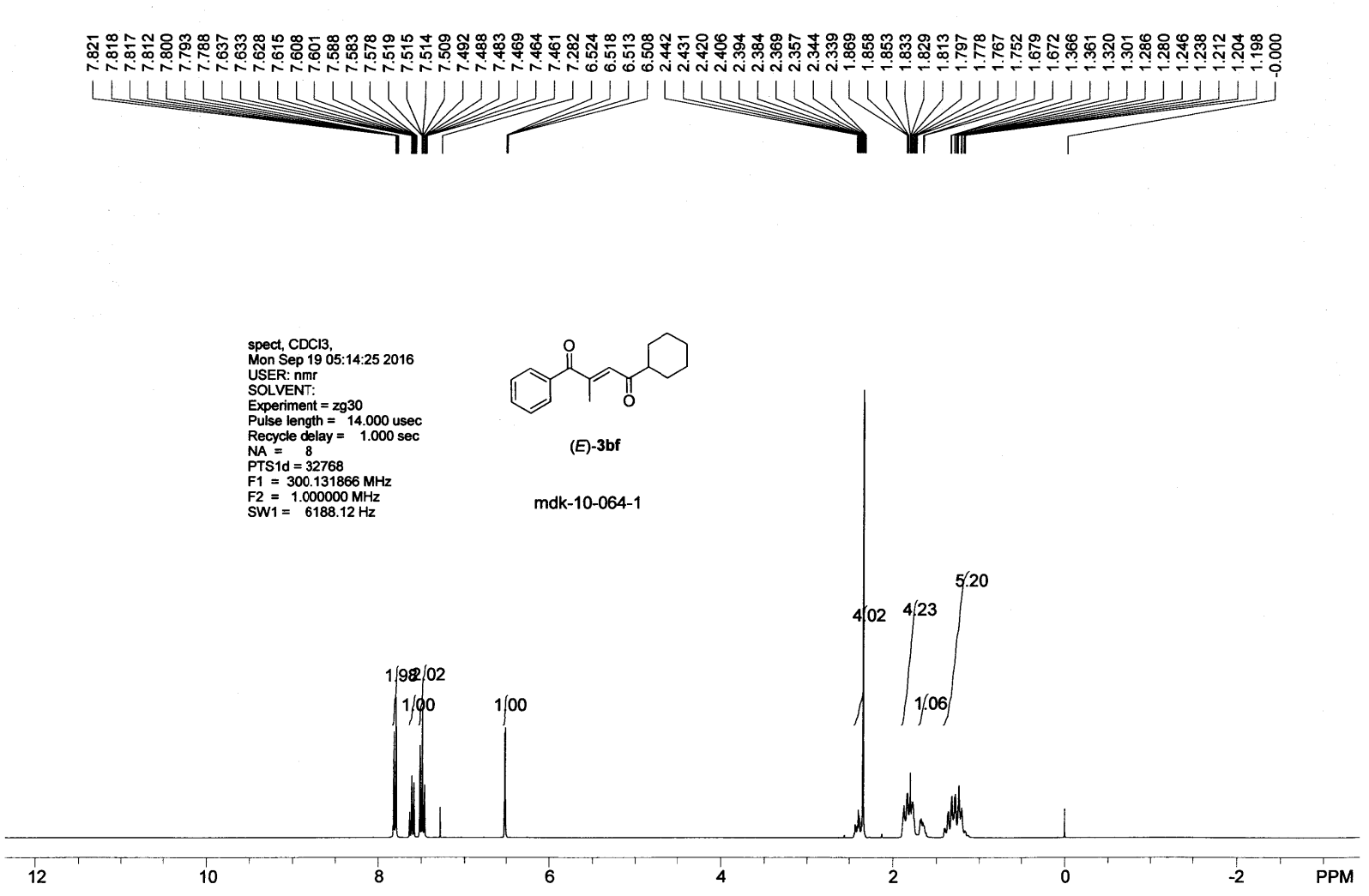

208.008
177.142
141.290
133.119
132.491
131.720
128.670
128.139
127.559
126.464
126.201
123.301
122.552
83.588
77.424
77.000
76.576
64.521
27.777
22.017
19.805
13.821
200
150
100
50
0PPM
spect, CDCl3,
Thu Dec 24 16:45:23 2015
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 7578
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-8-115-1
4R*,5S*-5ee
OH
H
O

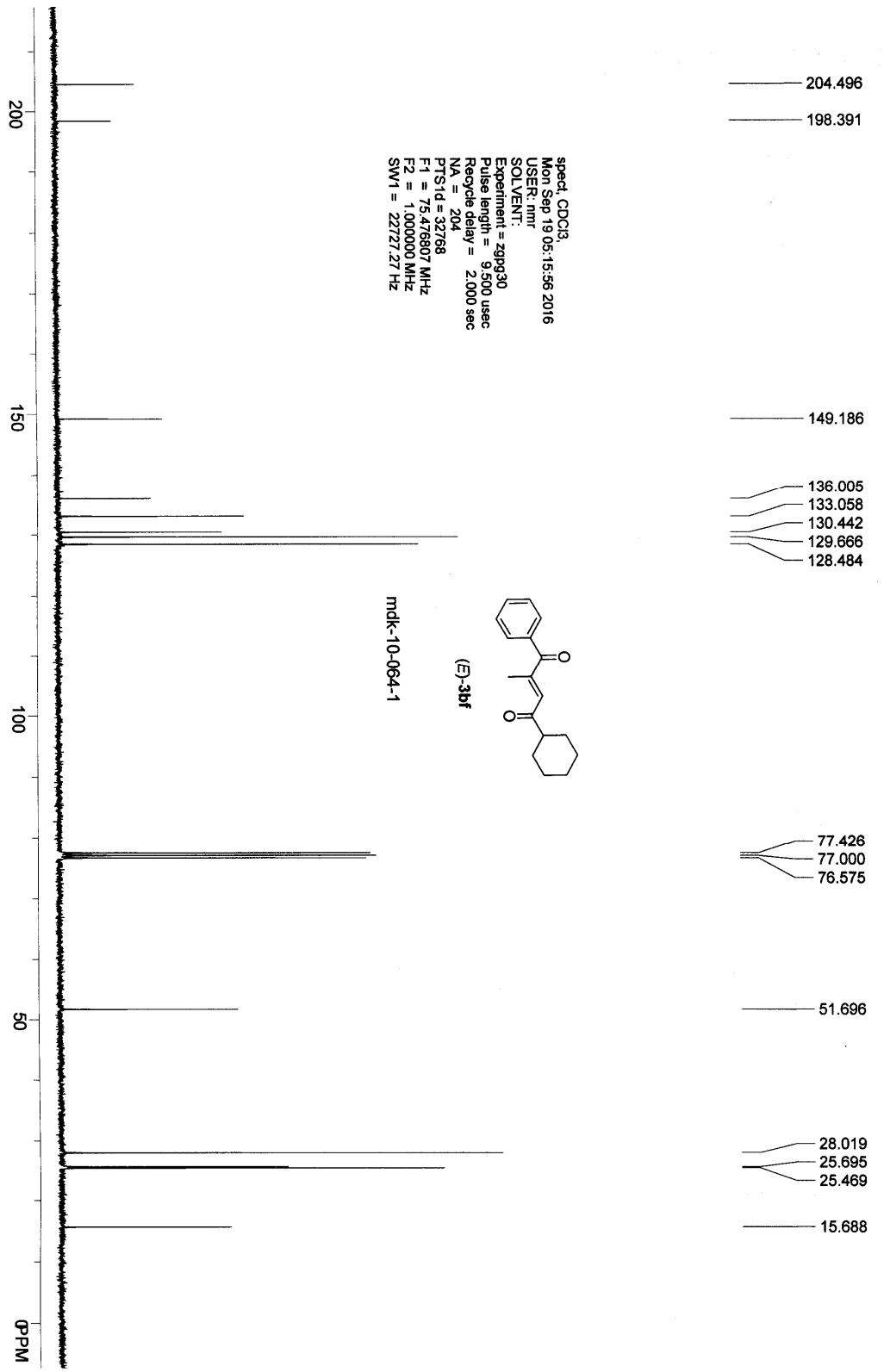

spect, CDCl3,
Fri Jan 01 01:56:06 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
4R*,5R*-5ee
mdk-8-115-2
OH
H
O
7.849
7.841
7.832
7.817
7.794
7.765
7.516
7.515
7.509
7.502
7.498
7.491
7.483
7.259
6.114
6.110
6.106
6.101
2.563
2.536
2.507
1.872
1.868
1.834
1.812
1.804
1.790
1.782
1.768
1.760
1.738
1.650
1.053
1.031
0.744
0.722
0.000
4.01
3.36
1.00
0.82
1.03
3.06
0.99
3.02
3.09
10
8
6
4
2
0
PPM

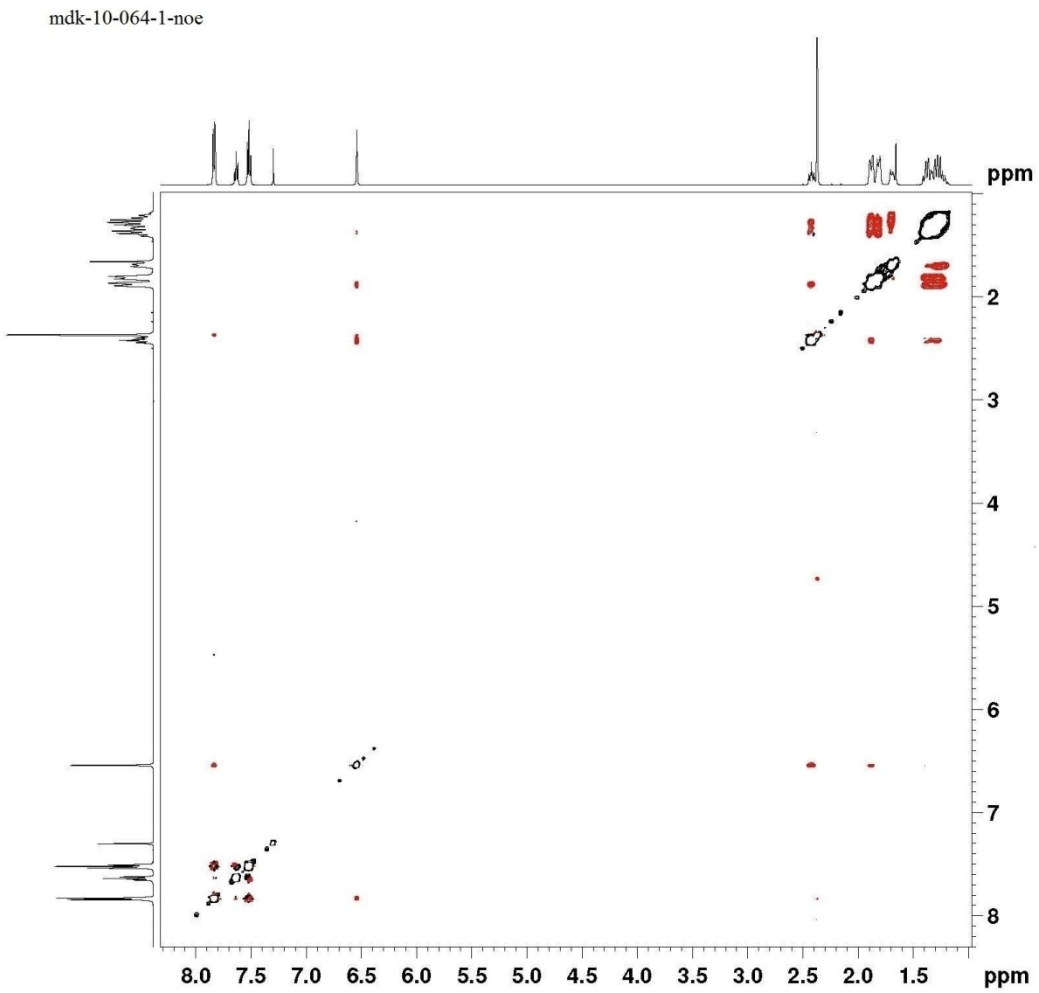

205.736
175.541
132.981
137.313
132.507
130.189
128.152
127.754
127.520
126.302
126.240
125.086
123.691
85.277
77.421
77.000
76.579
67.405
26.510
21.819
20.521
13.292
200
150
100
50
0 PPM
spect, CDCl3,
Thu Dec 24 08:27:59 2015
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 676
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-8-115-2
4R*,5R*-5ee
OH
O
H

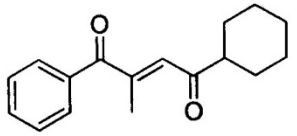

spect, CDCl3,
Tue Jan 26 15:17:37 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-9-010-1
(E)-3bf
2.01
1.02
2.07
1.00
4.10
4.39
1.19
5.79
PPM
10
8
6
4
2
0
7.819
7.814
7.809
7.798
7.791
7.786
7.635
7.631
7.626
7.614
7.606
7.599
7.586
7.582
7.577
7.518
7.514
7.512
7.506
7.490
7.486
7.468
7.462
7.459
7.263
6.516
6.511
6.505
6.501
2.426
2.416
2.401
2.390
2.379
2.365
2.353
2.342
2.337
1.870
1.828
1.793
1.770
1.669
1.567
1.406
1.358
1.320
1.284
1.238
1.211
0.000


spect, CDCl3,
Mon Jan 25 05:00:06 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 2615
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-9-010-1
(E)-3bf
O
O
O
204.569
198.469
149.266
136.076
133.106
130.486
129.730
128.545
77.421
77.000
76.579
51.780
28.079
25.760
25.538
15.757
200
150
100
50
0 PPM


7.821
7.818
7.817
7.812
7.800
7.793
7.788
7.637
7.633
7.628
7.615
7.608
7.601
7.588
7.583
7.578
7.519
7.515
7.514
7.509
7.492
7.488
7.483
7.469
7.464
7.461
7.282
6.524
6.518
6.513
6.508
2.442
2.431
2.420
2.406
2.394
2.384
2.369
2.357
2.344
2.339
1.869
1.858
1.853
1.833
1.829
1.813
1.797
1.778
1.767
1.752
1.679
1.672
1.366
1.361
1.320
1.301
1.286
1.280
1.246
1.238
1.212
1.204
1.198
-0.000
spect, CDCl3,
Mon Sep 19 05:14:25 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
O
O
O
(E)-3bf
mdk-10-064-1
1.98
2.02
1.00
1.00
4.02
4.23
5.20
1.06
12
10
8
6
4
2
0
-2
PPM

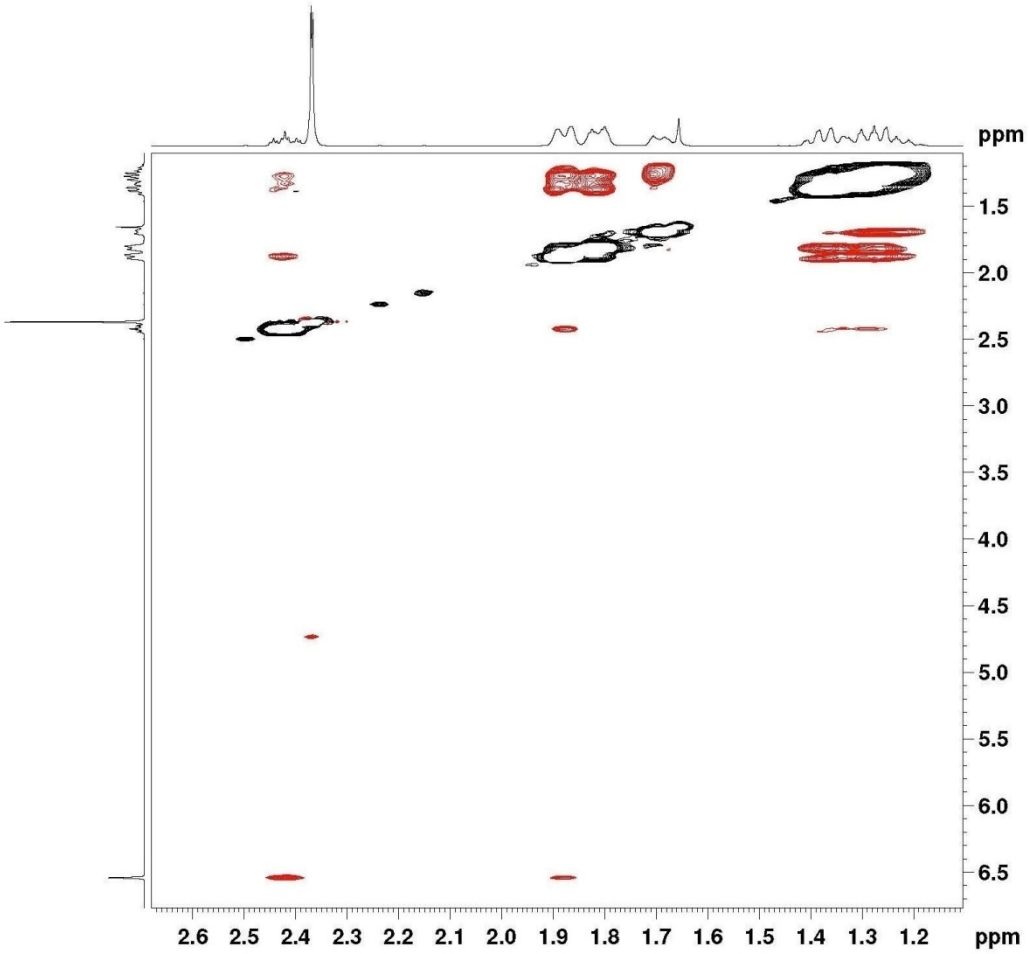

spect, CDCl3,
Mon Sep 19 05:15:56 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 204
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-10-064-1
(E)-3bf
204.496
198.391
149.186
136.005
133.058
130.442
129.666
128.484
77.426
77.000
76.575
51.696
28.019
25.695
25.469
15.688
200
150
100
50
0PPM

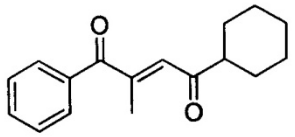

mdk-10-064-1-noe
ppm
2
3
4
5
6
7
8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


O
O

(*E*)-**3bf**

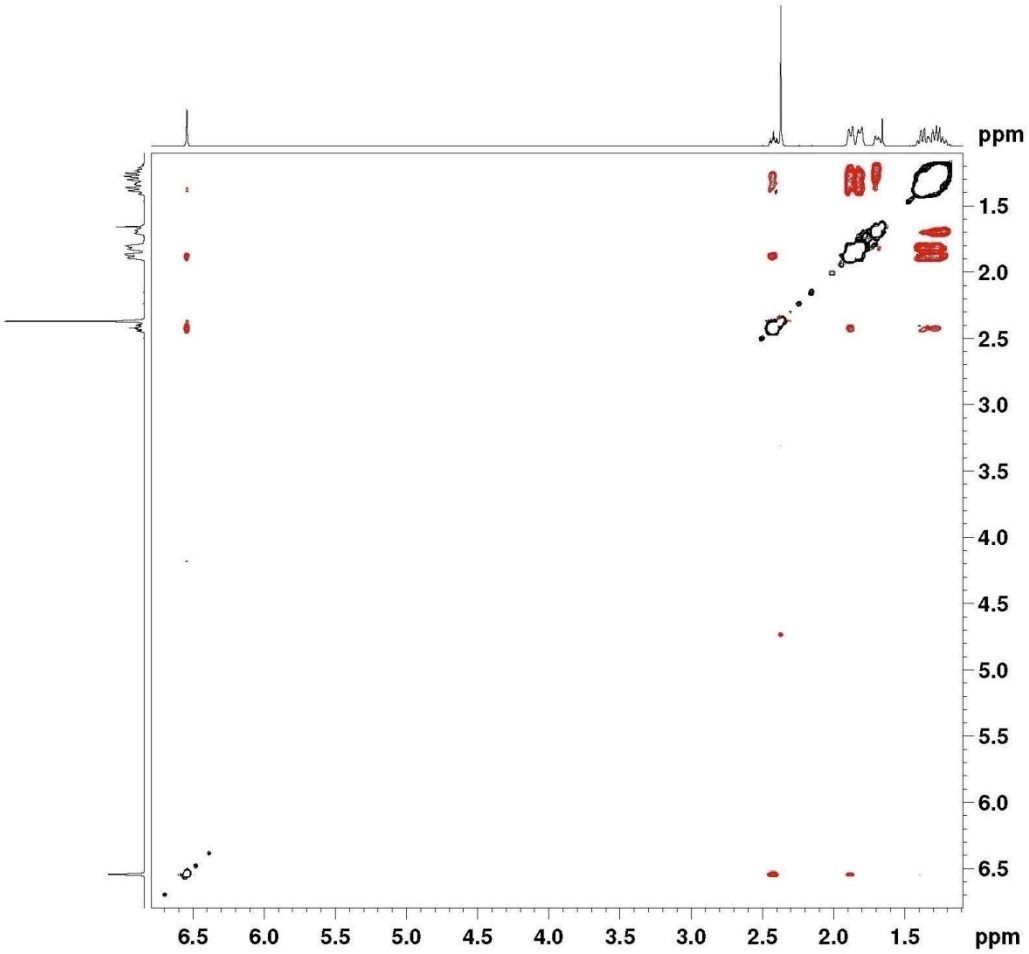
mdk-10-064-1-noe

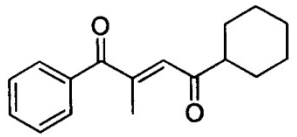




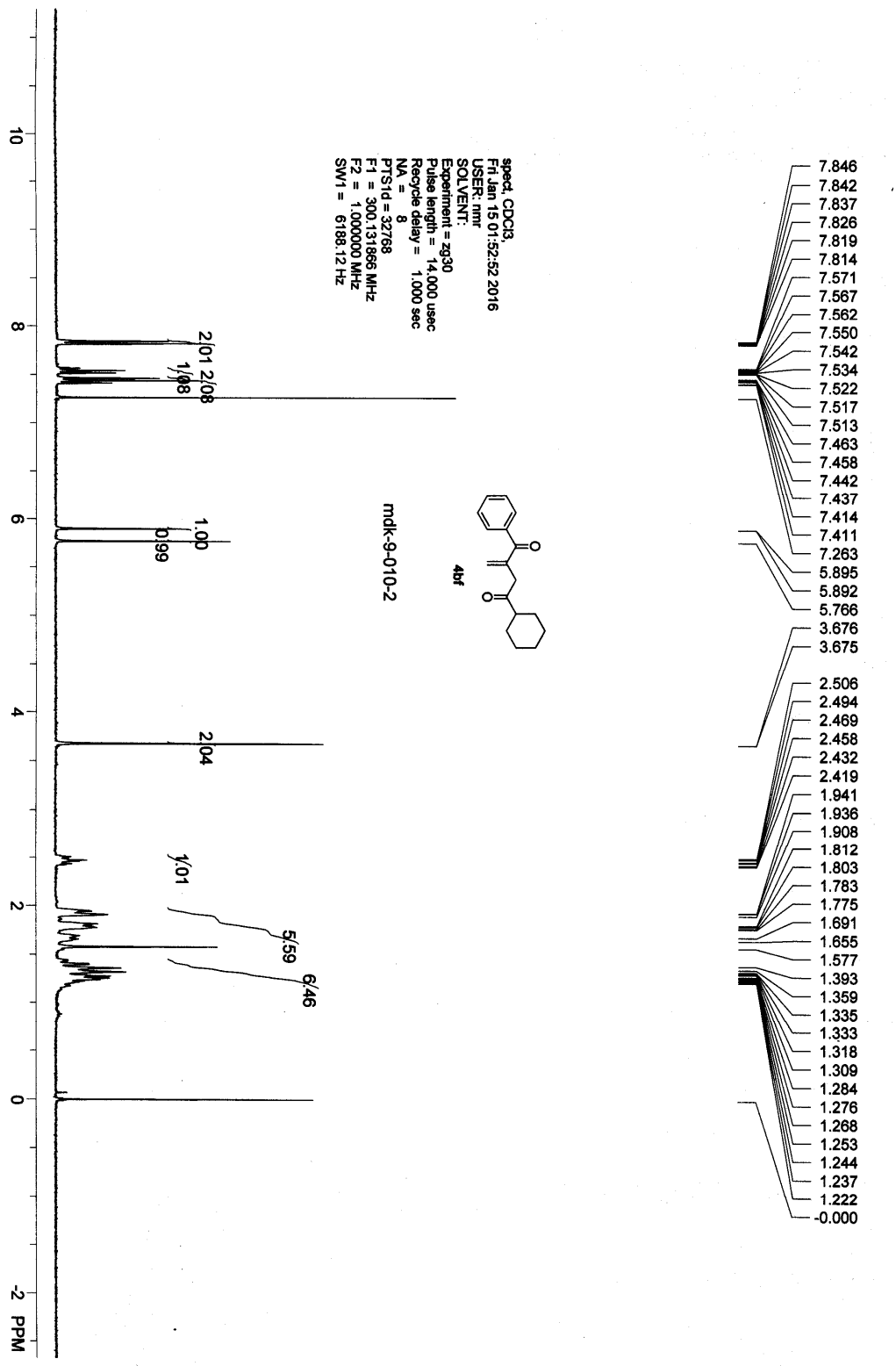
(*E*)-**3bf**

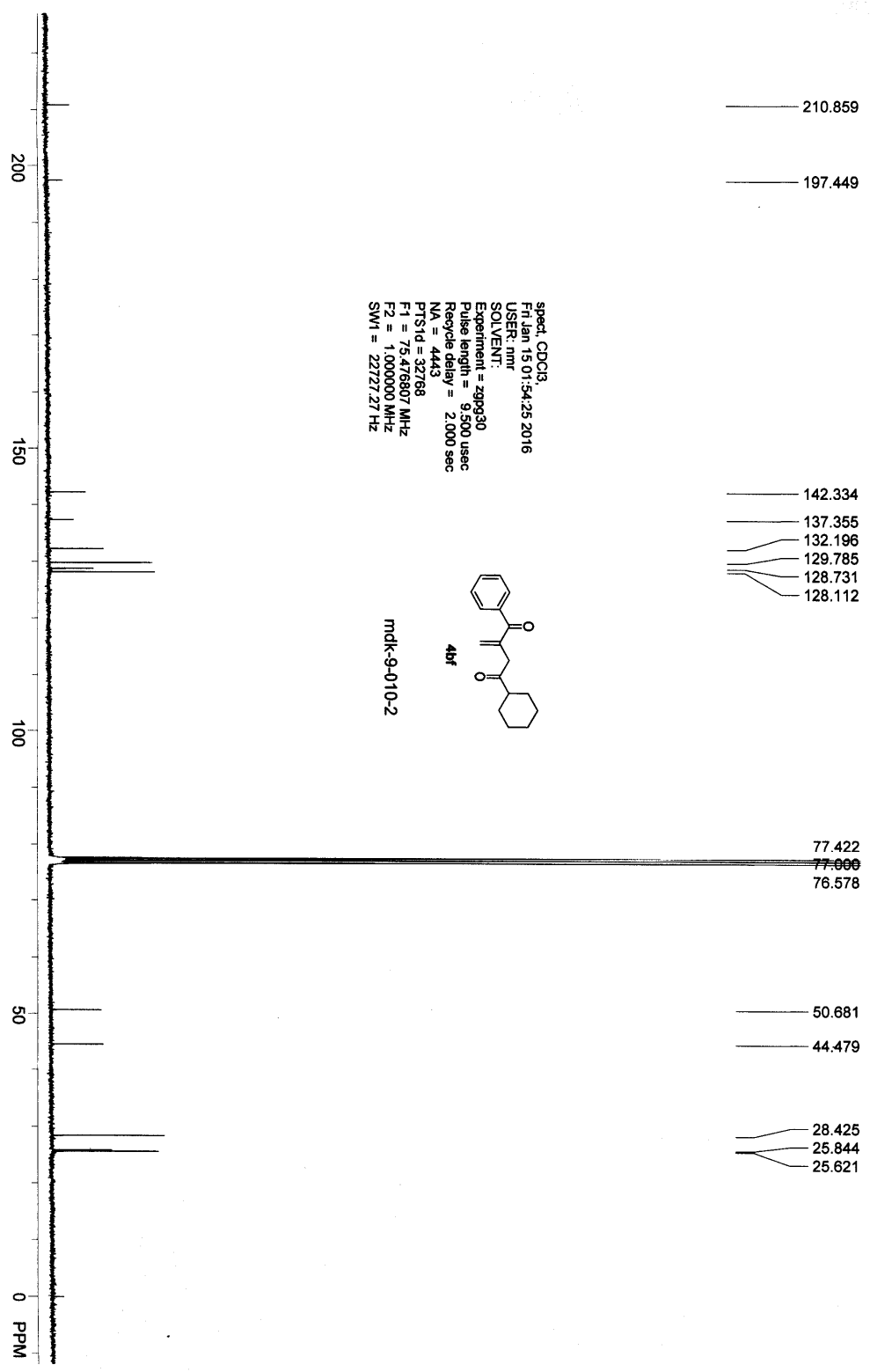
mdk-10-064-1-noe

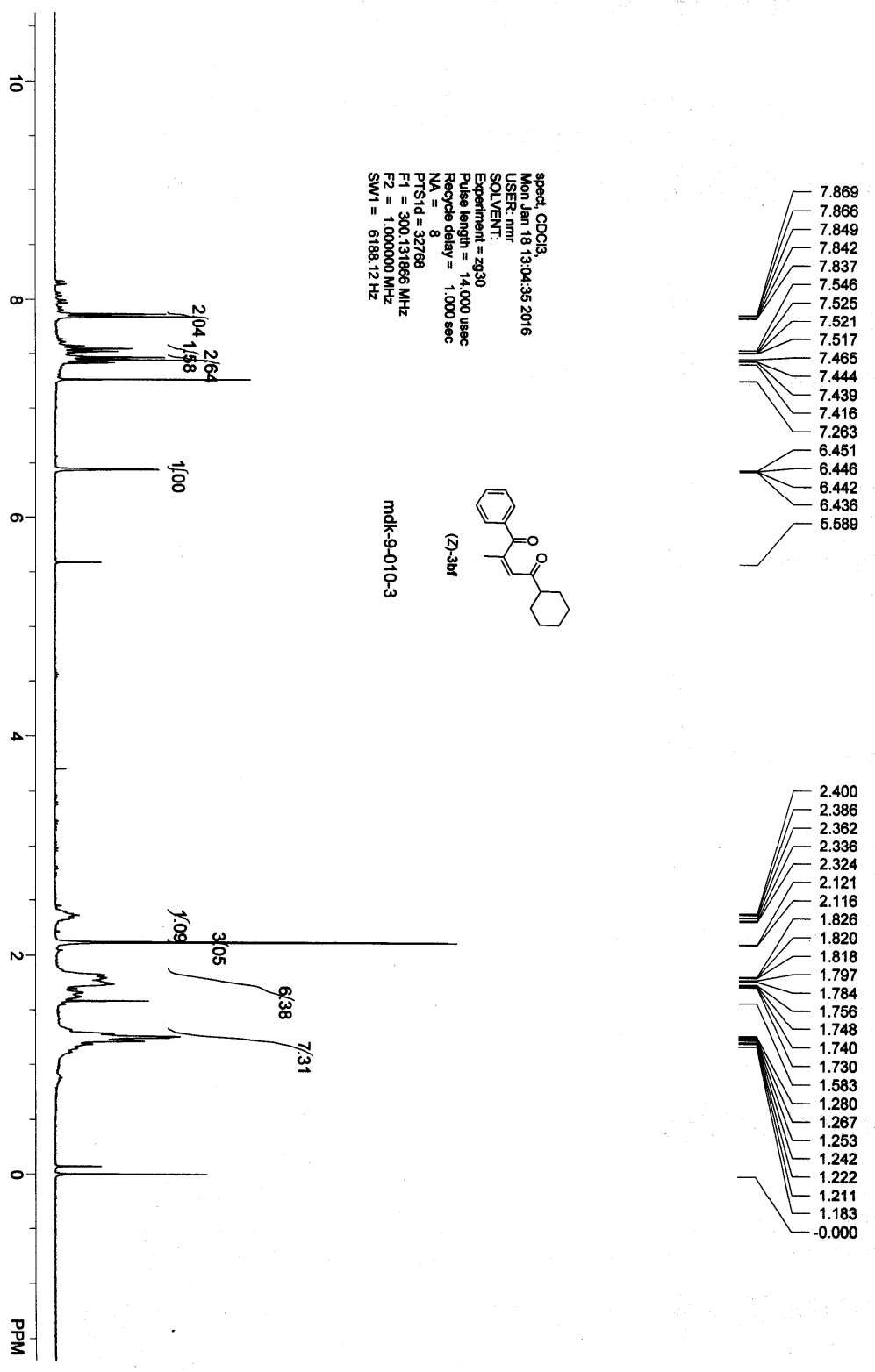


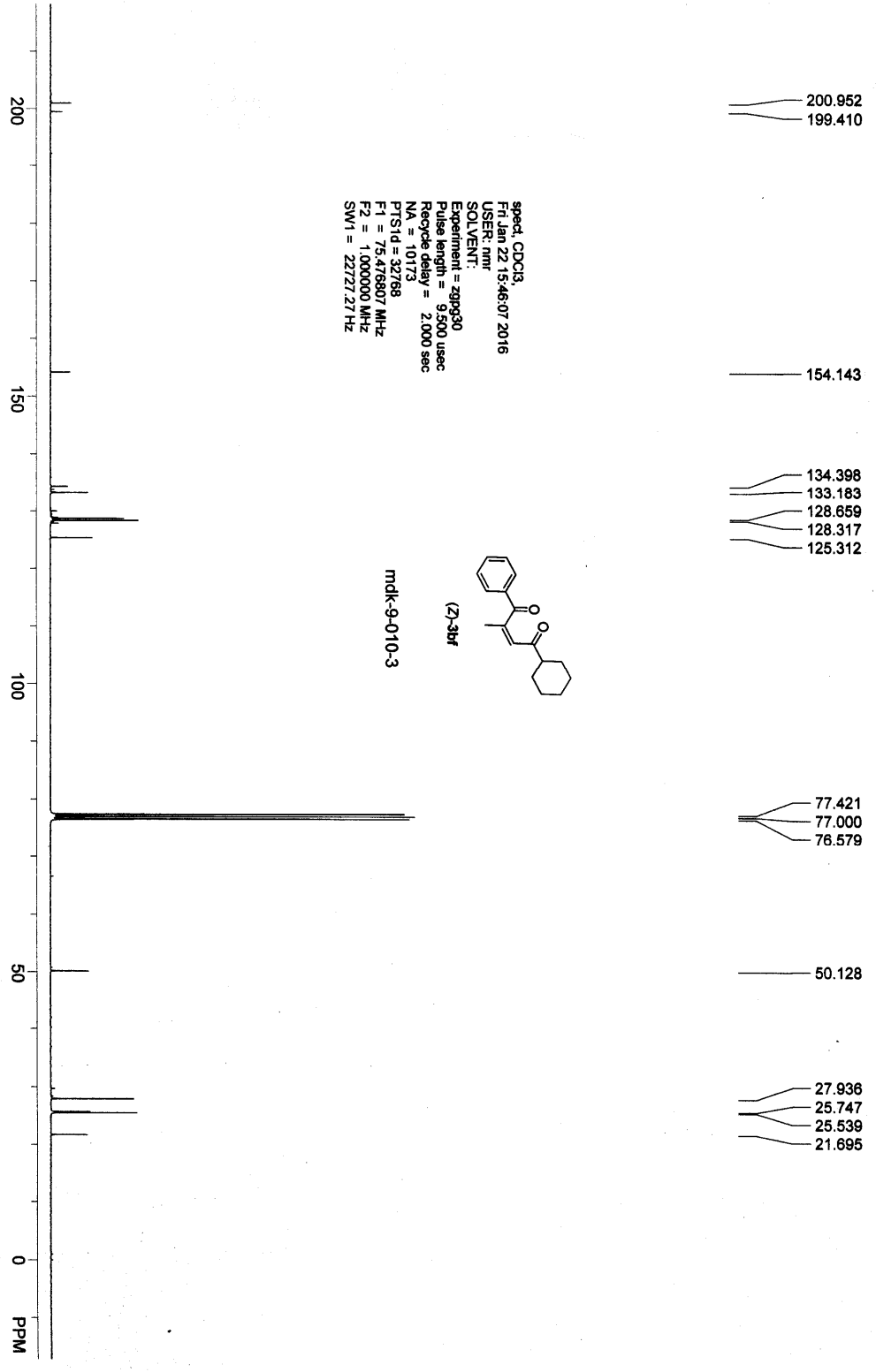


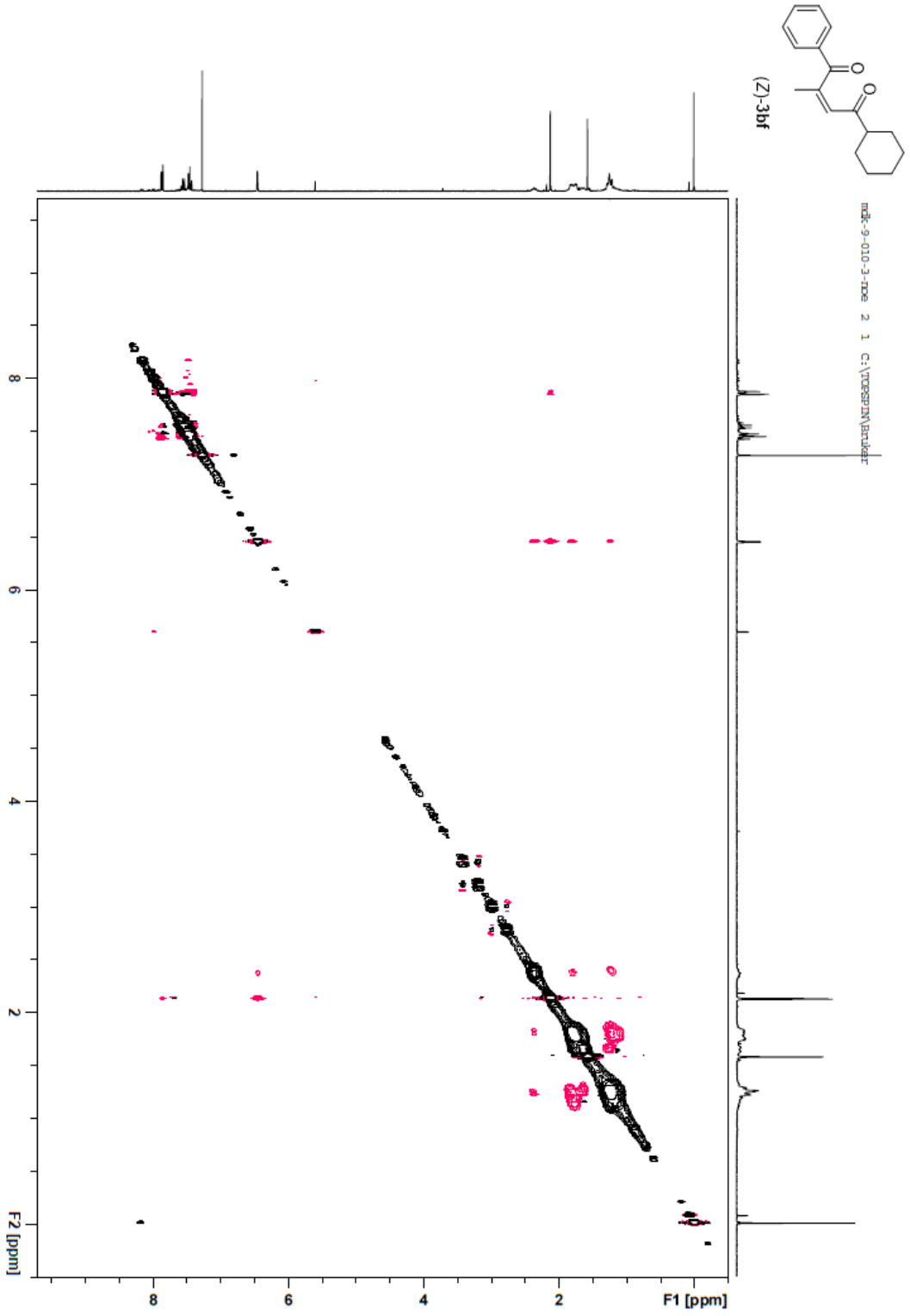
(*E*)-3bf

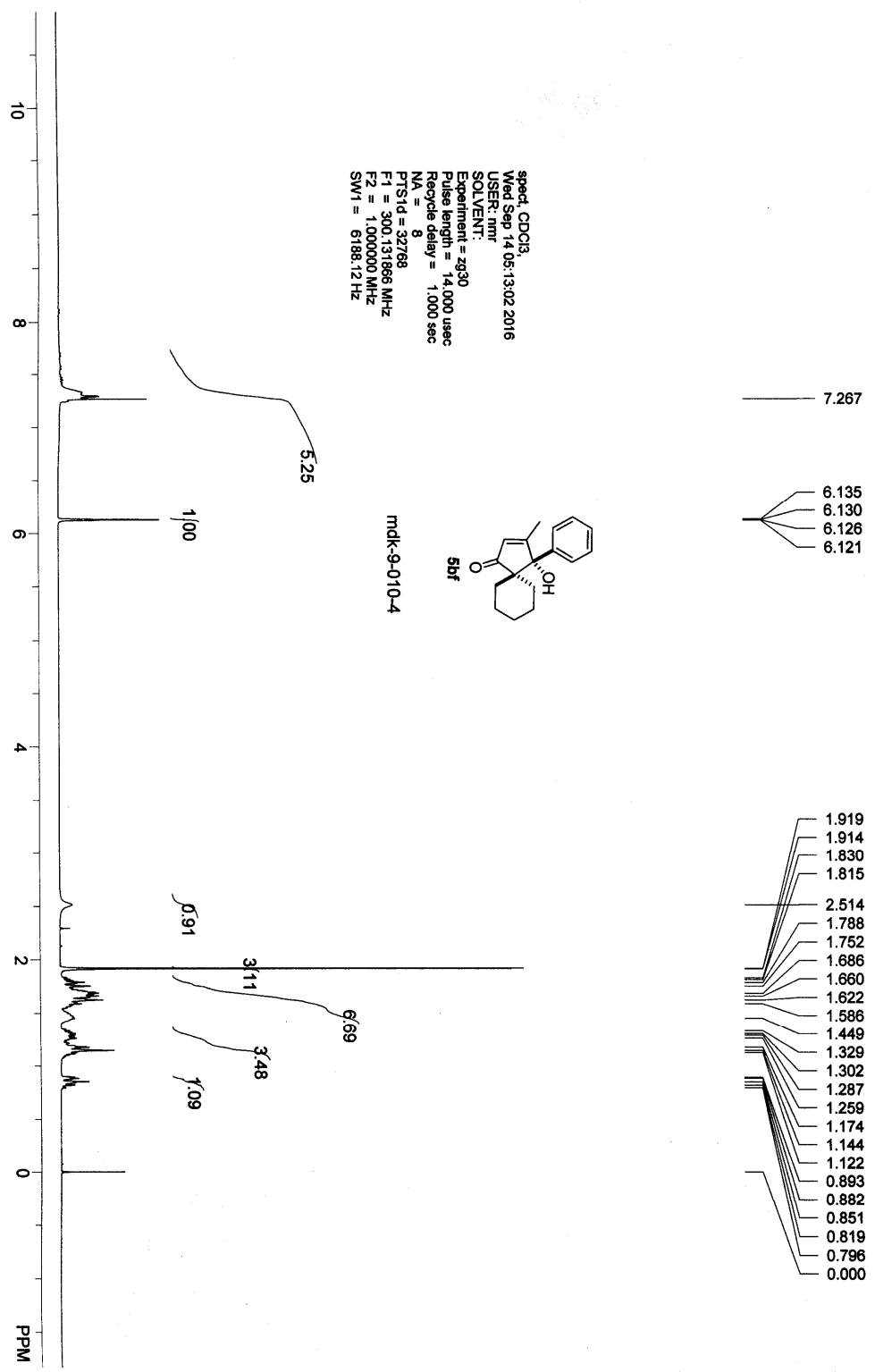

spect, CDCl3,
Fri Jan 15 01:52:52 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-9-010-2
4bf
2.01
2.08
1.08
1.00
0.99
2.04
1.01
5.59
6.46
10
8
6
4
2
0
-2
PPM
7.846
7.842
7.837
7.826
7.819
7.814
7.571
7.567
7.562
7.550
7.542
7.534
7.522
7.517
7.513
7.463
7.458
7.442
7.437
7.414
7.411
7.263
5.895
5.892
5.766
3.676
3.675
2.506
2.494
2.469
2.458
2.432
2.419
1.941
1.936
1.908
1.812
1.803
1.783
1.775
1.691
1.655
1.577
1.393
1.359
1.335
1.333
1.318
1.309
1.284
1.276
1.268
1.253
1.244
1.237
1.222
-0.000

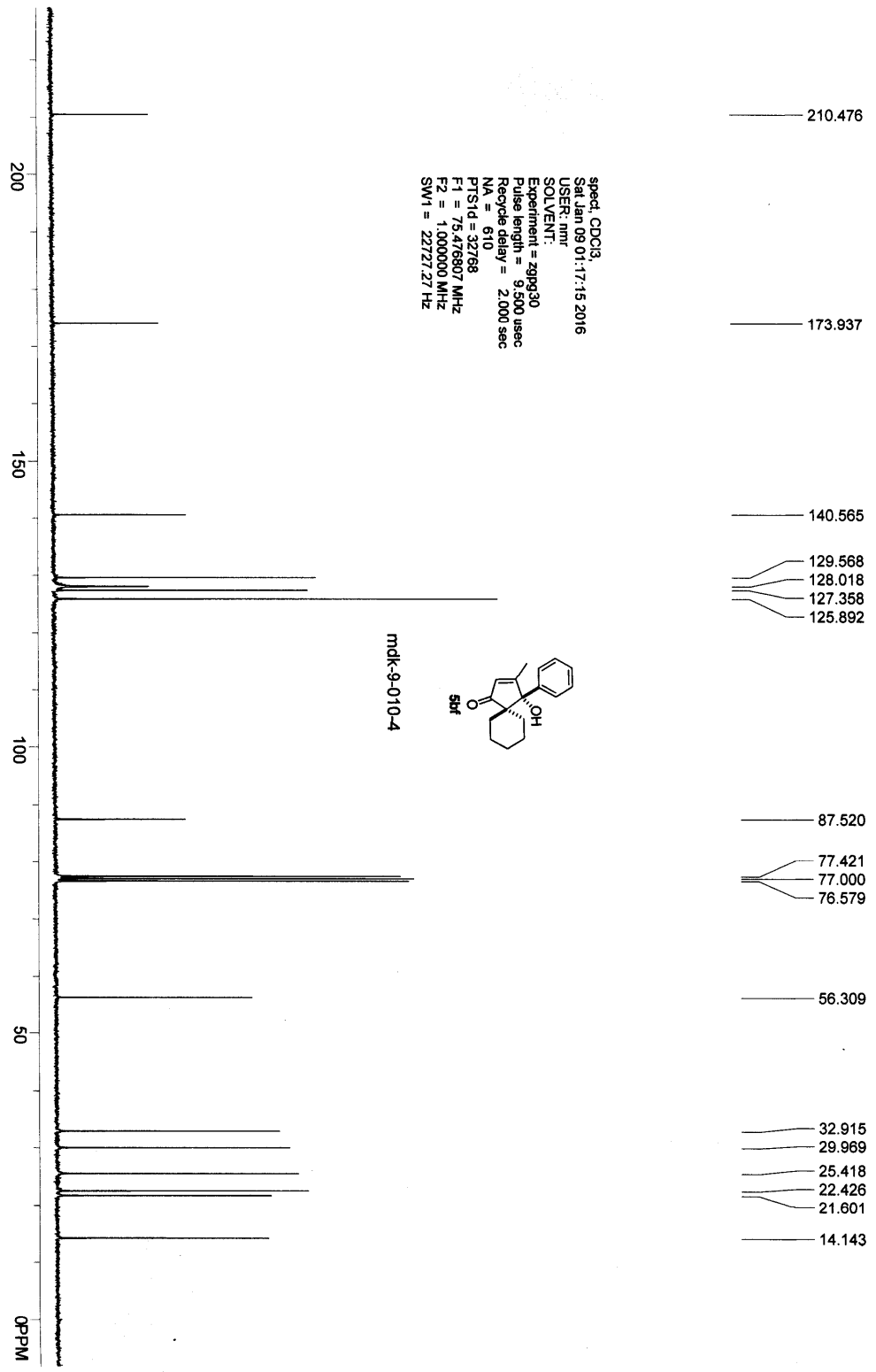

210.859
197.449
142.334
137.355
132.196
129.785
128.731
128.112
77.422
77.000
76.578
50.681
44.479
28.425
25.844
25.621
200
150
100
50
0 PPM
spect, CDCl3,
Fri Jan 15 01:54:25 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 4443
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-9-010-2
4bf

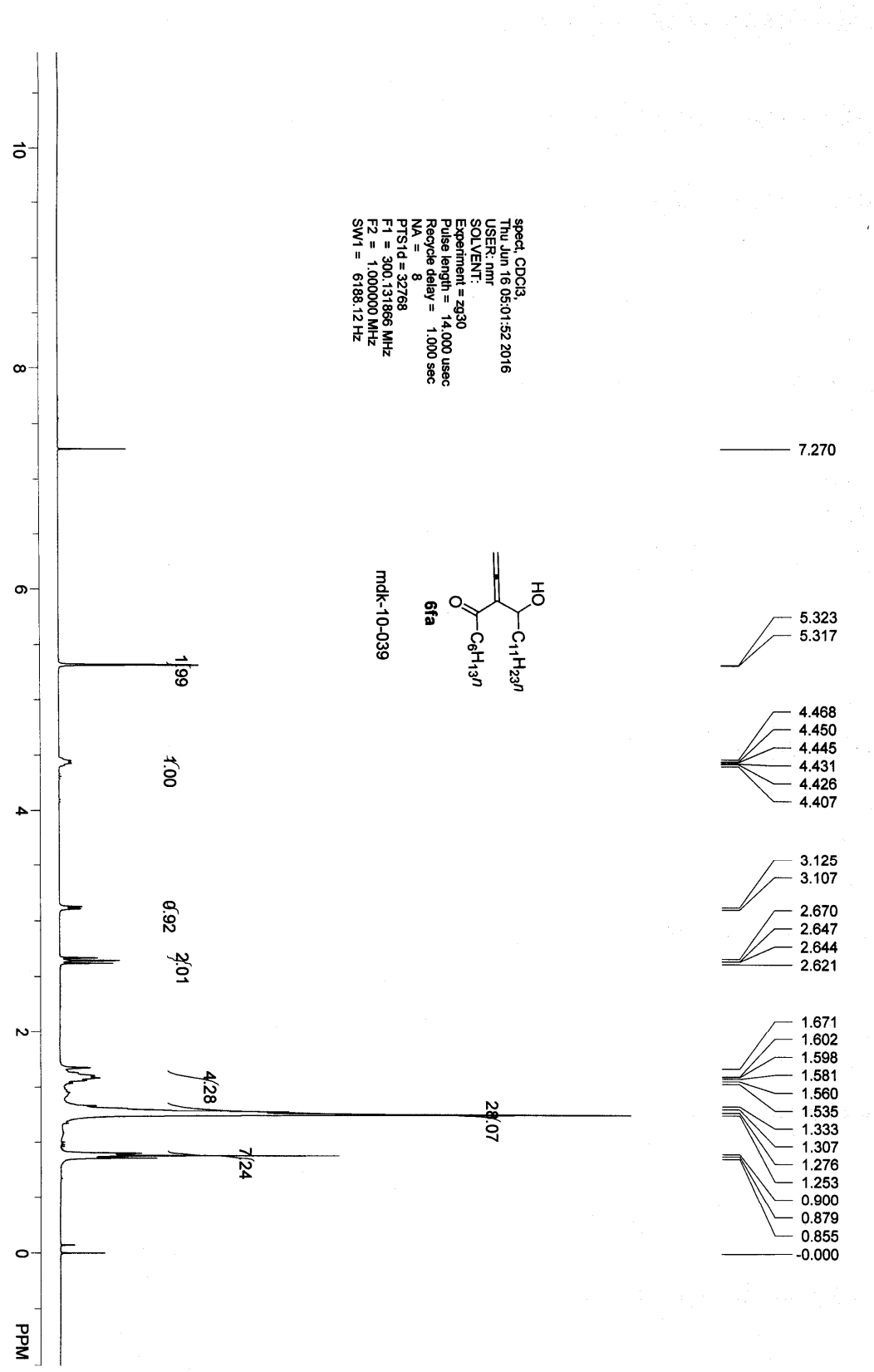

spect, CDCl3,
Mon Jan 18 13:04:35 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-9-010-3
(Z)-3bf
7.869
7.866
7.849
7.842
7.837
7.546
7.525
7.521
7.517
7.465
7.444
7.439
7.416
7.263
6.451
6.446
6.442
6.436
5.589
2.400
2.386
2.362
2.336
2.324
2.121
2.116
1.826
1.820
1.818
1.797
1.784
1.756
1.748
1.740
1.730
1.583
1.280
1.267
1.253
1.242
1.222
1.211
1.183
-0.000
2.04
1.88
2.64
1.00
1.09
3.05
6.38
7.31
10
8
6
4
2
0
PPM

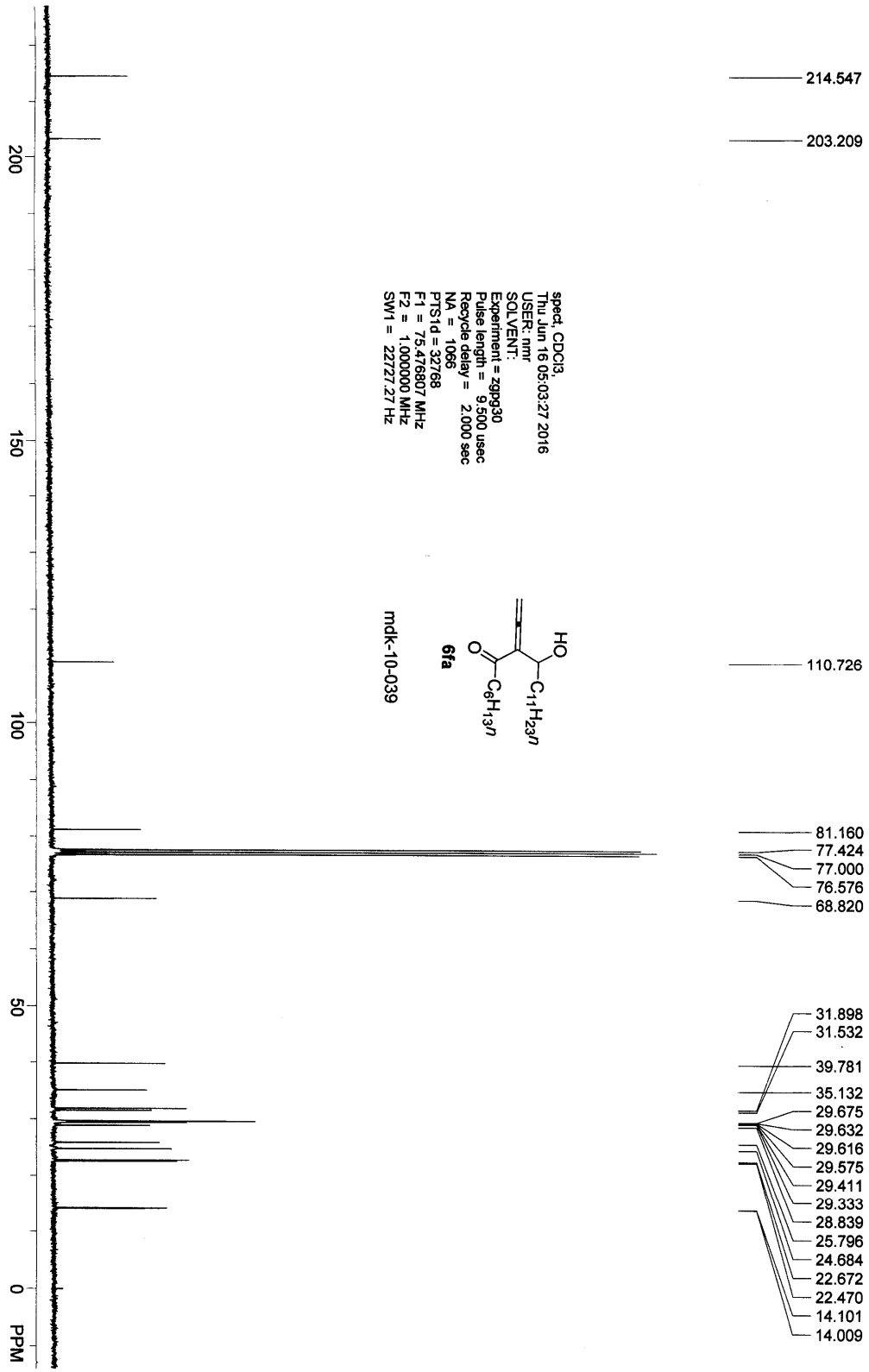

200.952
199.410
154.143
134.398
133.183
128.659
128.317
125.312
77.421
77.000
76.579
50.128
27.936
25.747
25.539
21.695
200
150
100
50
0
PPM
spect, CDCl3,
Fri Jan 22 15:46:07 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 10173
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-9-010-3
(Z)-3bf

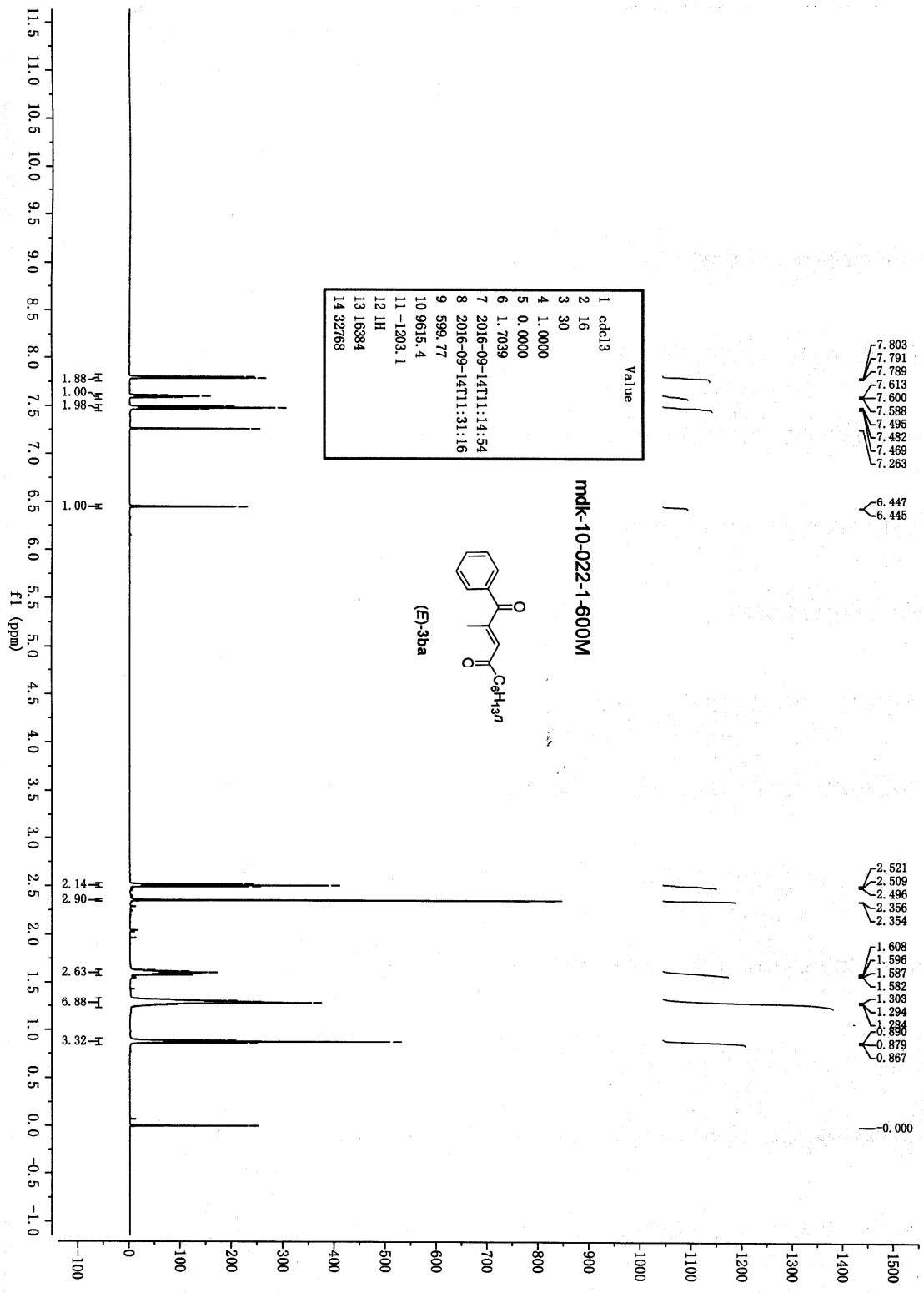

(Z)-3bf
mdk-9-010-3-roe 2 1 C:\nosqnp\Bruker
F2 [ppm]
F1 [ppm]
8
6
4
2

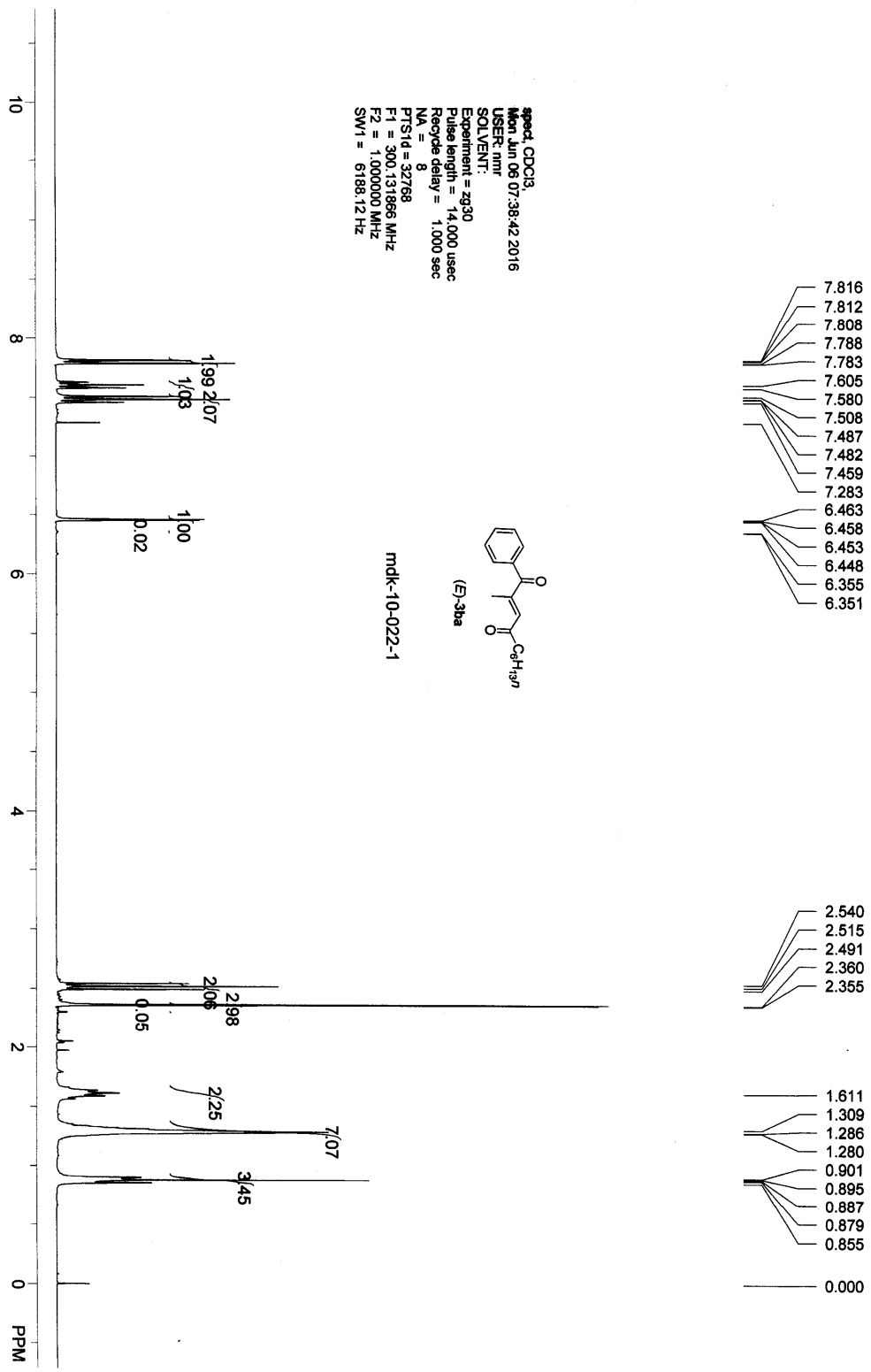

spect, CDCl3,
Wed Sep 14 05:13:02 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-9-010-4
5bf
OH
O
7.267
6.135
6.130
6.126
6.121
1.919
1.914
1.830
1.815
2.514
1.788
1.752
1.686
1.660
1.622
1.586
1.449
1.329
1.302
1.287
1.259
1.174
1.144
1.122
0.893
0.882
0.851
0.819
0.796
0.000
5.25
1.00
0.91
3.11
6.69
3.48
1.09
10
8
6
4
2
0
PPM

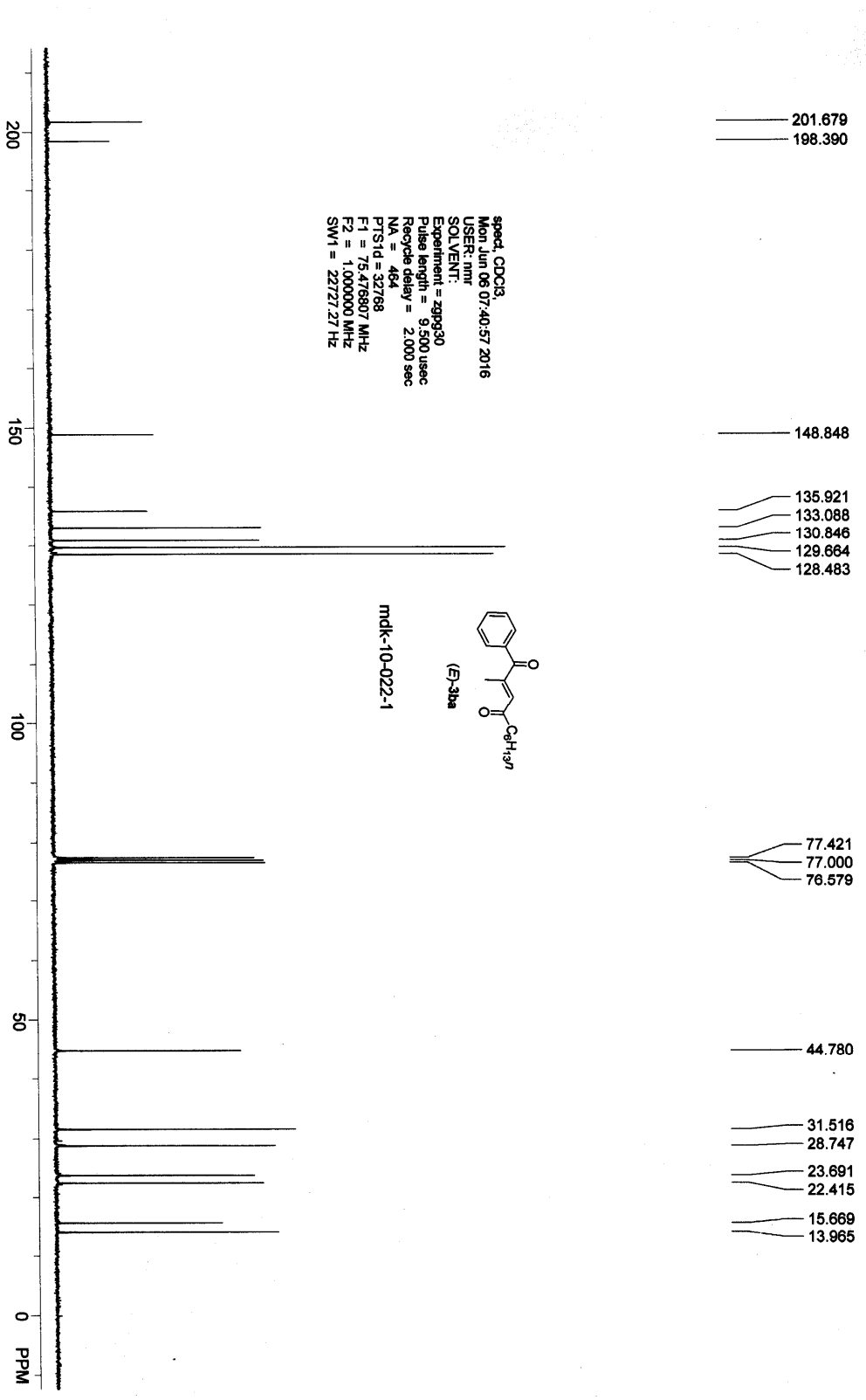

spect, CDCl3,
Sat Jan 09 01:17:15 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 610
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-9-010-4
5bf
OH
O
210.476
173.937
140.565
129.568
128.018
127.358
125.892
87.520
77.421
77.000
76.579
56.309
32.915
29.969
25.418
22.426
21.601
14.143
200
150
100
50
0PPM

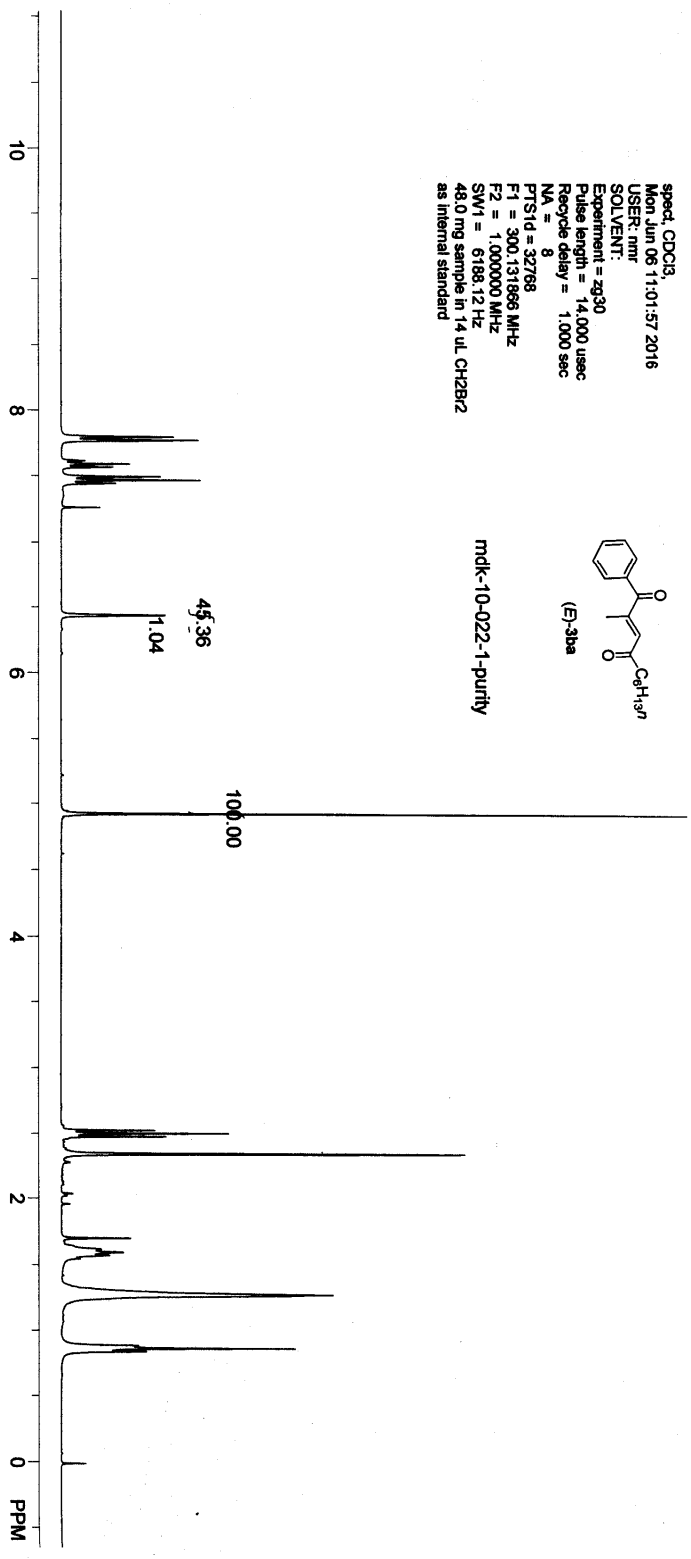

spect, CDCl3,
Thu Jun 16 05:01:52 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-10-039
6fa
HO
O
C11H23n
C6H13n
7.270
5.323
5.317
4.468
4.450
4.445
4.431
4.426
4.407
3.125
3.107
2.670
2.647
2.644
2.621
1.671
1.602
1.598
1.581
1.560
1.535
1.333
1.307
1.276
1.253
0.900
0.879
0.855
-0.000
1.99
1.00
0.92
2.01
4.28
28.07
7.24
10
8
6
4
2
0
PPM

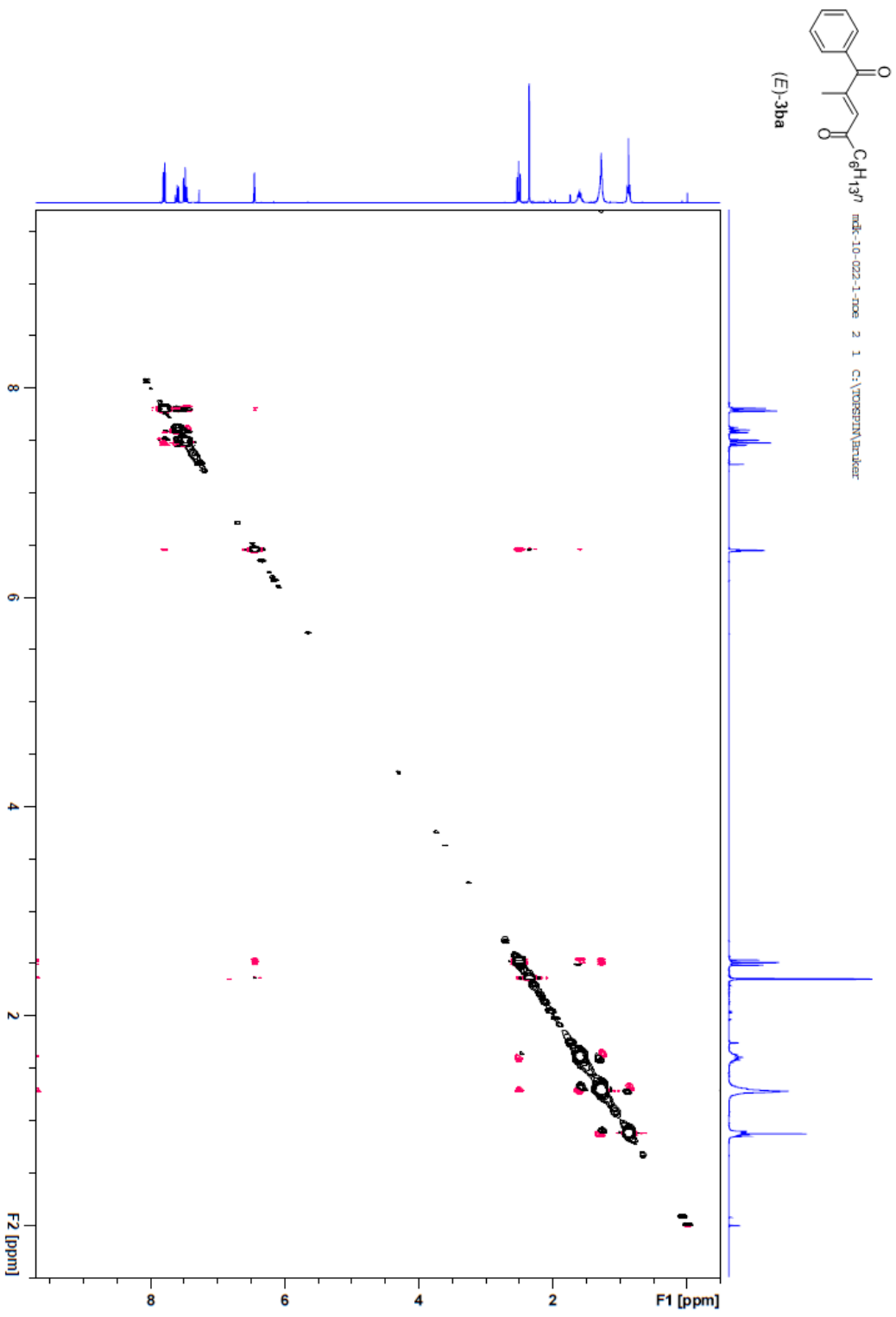

214.547
203.209
110.726
81.160
77.424
77.000
76.576
68.820
31.898
31.532
39.781
35.132
29.675
29.632
29.616
29.575
29.411
29.333
28.839
25.796
24.684
22.672
22.470
14.101
14.009
200
150
100
50
0
PPM
spect, CDCl3,
Thu Jun 16 05:03:27 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 1066
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-10-039
6fa
HO
O
C6H13n
C11H23n

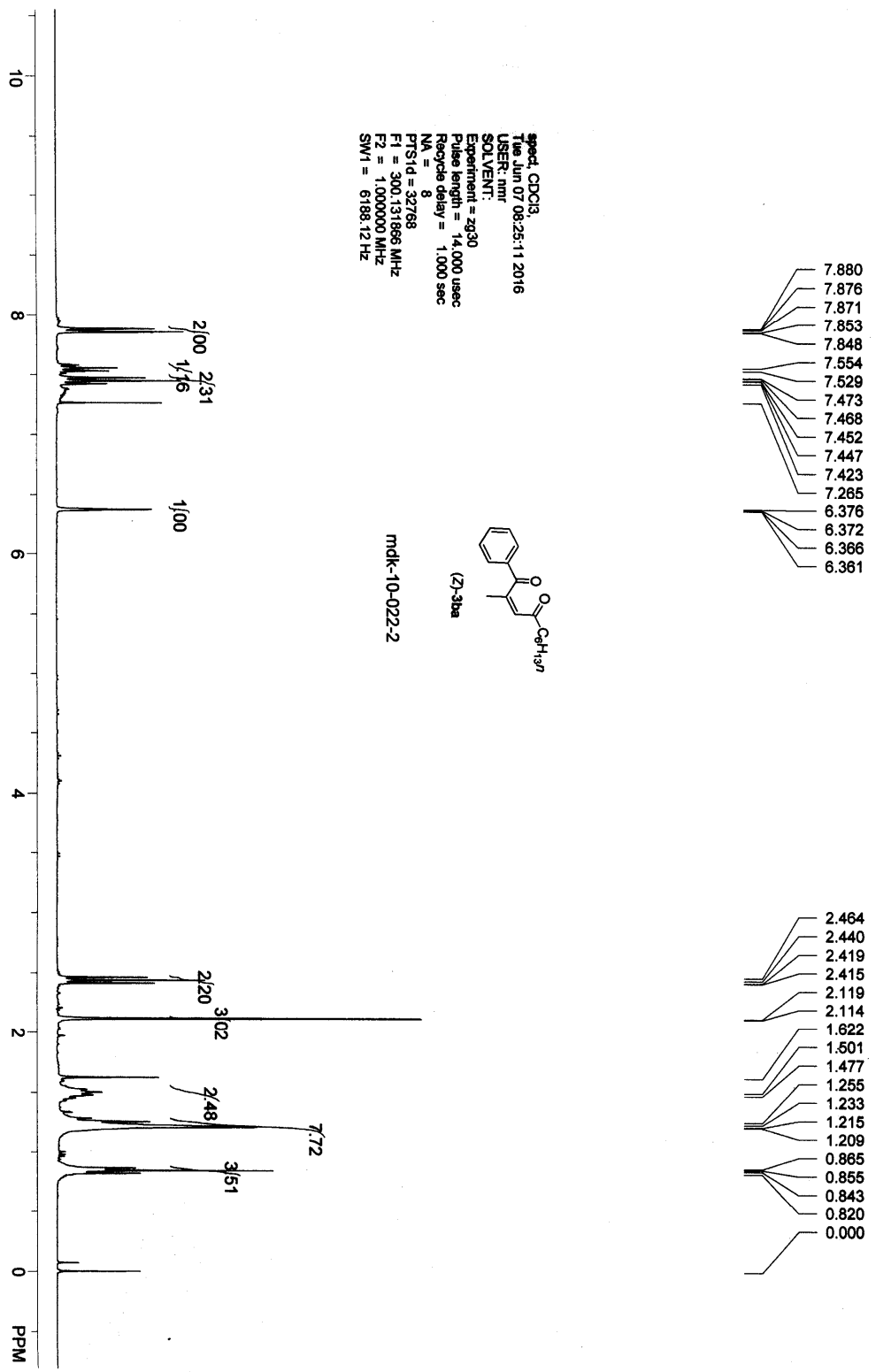

mdk-10-022-1-600M
(E)-3ba
Value
1 cdcl3
2 16
3 30
4 1.0000
5 0.0000
6 1.7039
7 2016-09-14T11:14:54
8 2016-09-14T11:31:16
9 599.77
10 9615.4
11 -1203.1
12 1H
13 16384
14 32768
7.803
7.791
7.789
7.613
7.600
7.588
7.495
7.482
7.469
7.263
6.447
6.445
2.521
2.509
2.496
2.356
2.354
1.608
1.596
1.587
1.582
1.303
1.294
1.284
0.890
0.879
0.867
0.000
1.88
1.00
1.98
1.00
2.14
2.90
2.63
6.88
3.32
f1 (ppm)

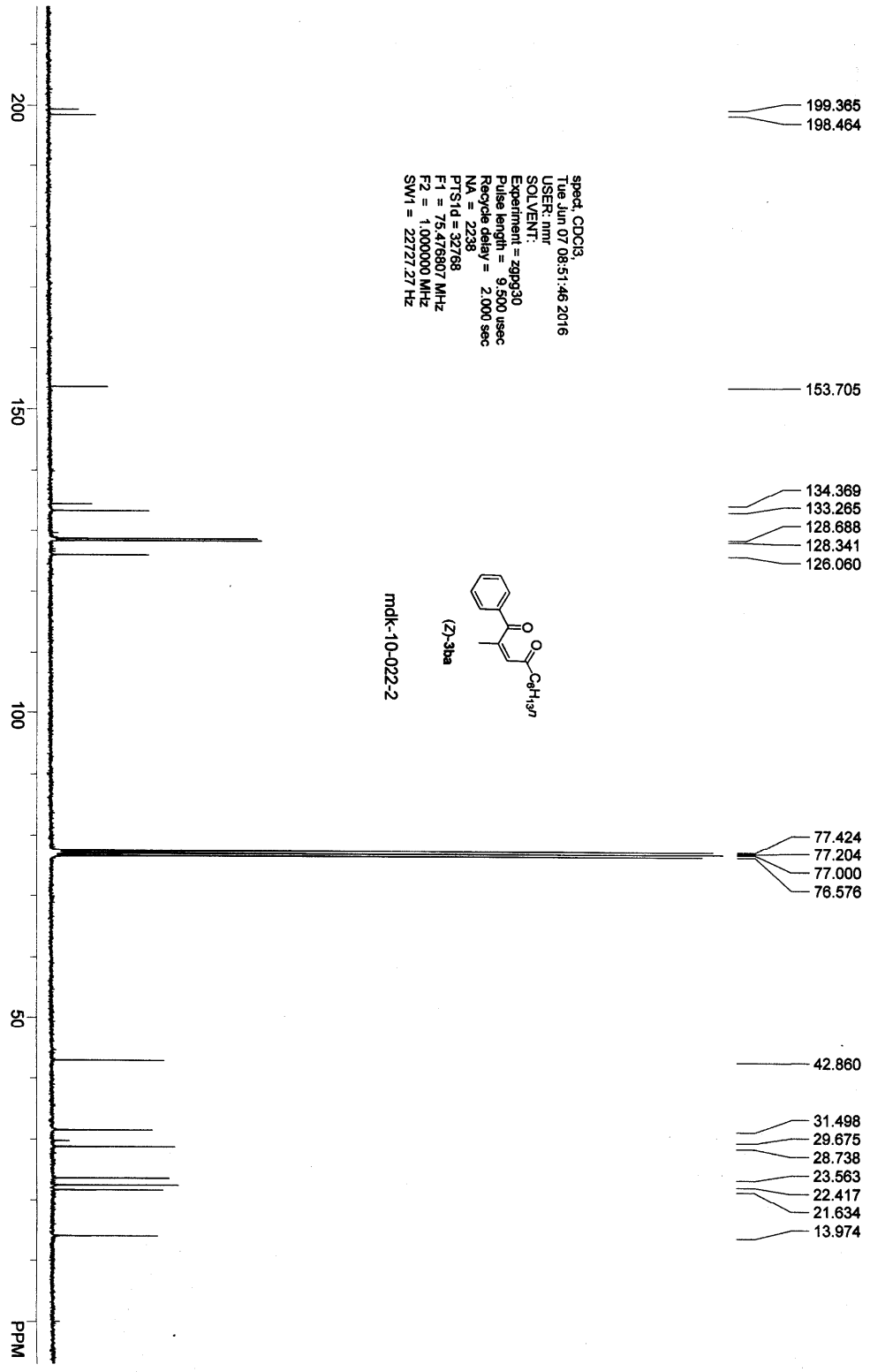

spect, CDCl3,
Mon Jun 06 07:38:42 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.1318 66 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-10-022-1
(E)-3ba
C9H13N
7.816
7.812
7.808
7.788
7.783
7.605
7.580
7.508
7.487
7.482
7.459
7.283
6.463
6.458
6.453
6.448
6.355
6.351
2.540
2.515
2.491
2.360
2.355
1.611
1.309
1.286
1.280
0.901
0.895
0.887
0.879
0.855
0.000
1.99
2.07
1.03
1.00
0.02
2.06
2.98
0.05
2.25
7.07
3.45
10
8
6
4
2
0
PPM

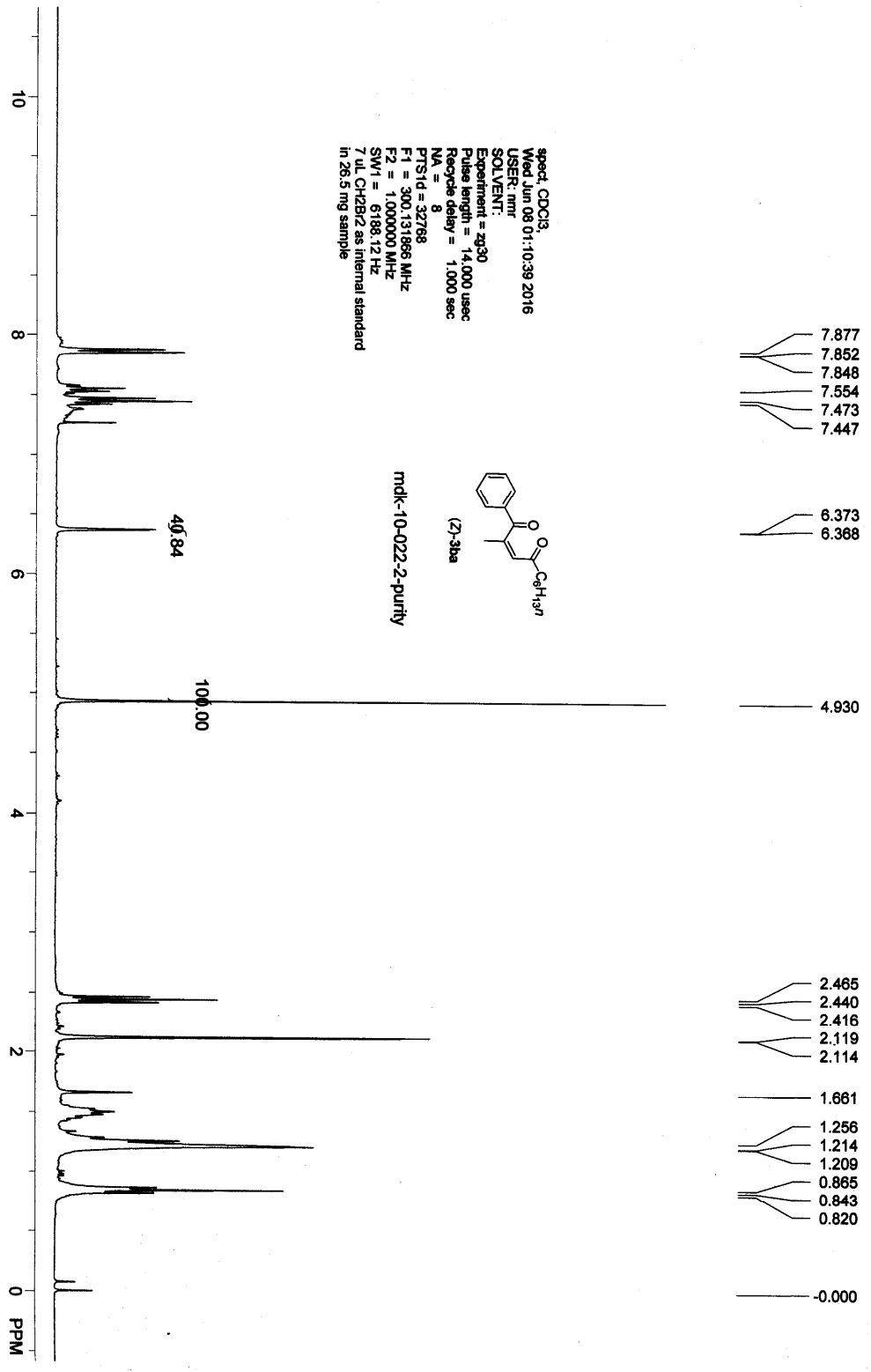

spect, CDCl3
Mon Jun 06 07:40:57 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 464
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-10-022-1
(E)-3ba
C6H13N7
201.679
198.390
148.848
135.921
133.088
130.846
129.664
128.483
77.421
77.000
76.579
44.780
31.516
28.747
23.691
22.415
15.669
13.965
200
150
100
50
0
PPM

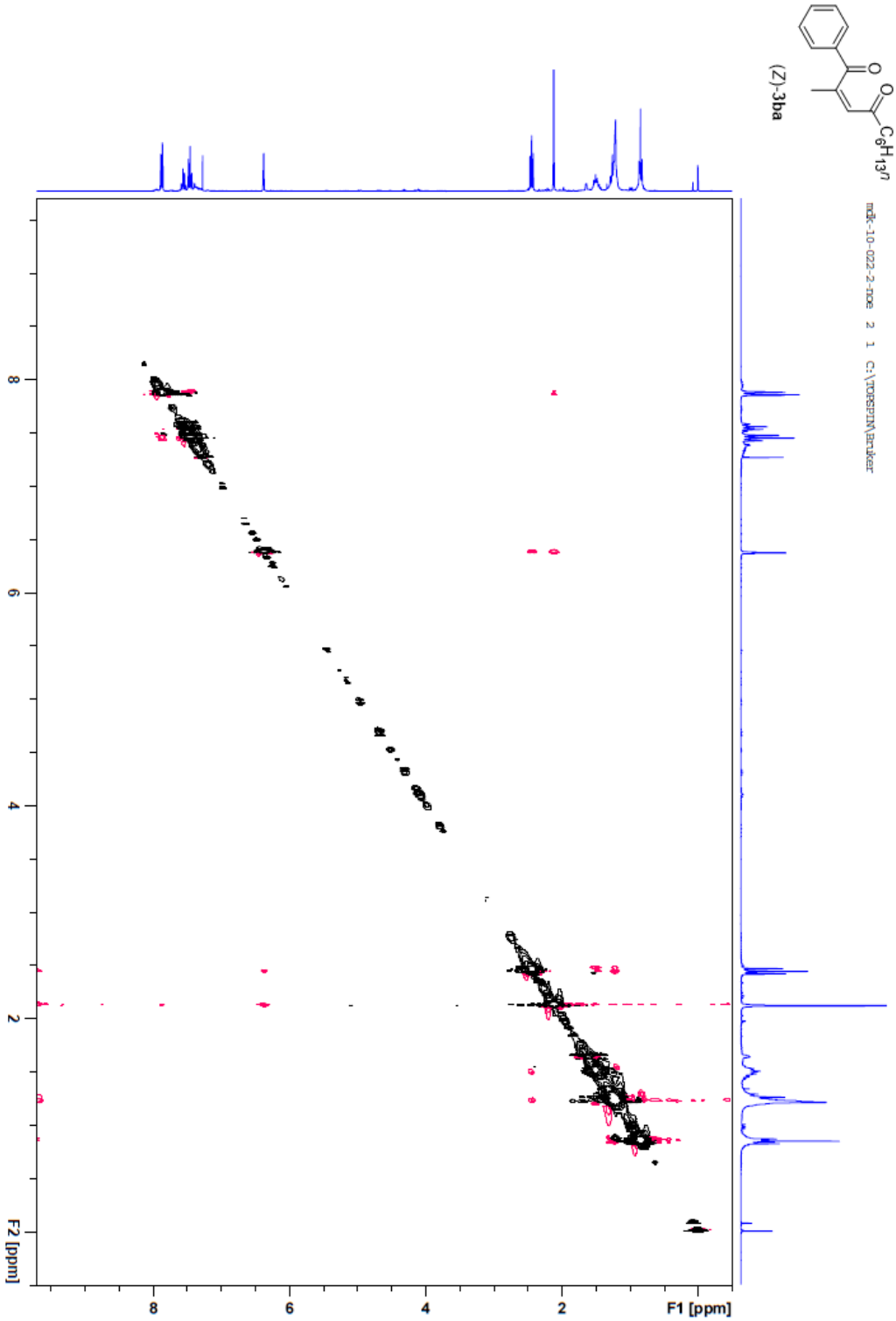

spect_CDCl3_
Mon Jun 06 11:01:57 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
48.0 mg sample in 14 uL CH2Br2
as internal standard
(E)-3ba
mdk-10-022-1-purity
45.36
1.04
100.00
10
8
6
4
2
0
PPM

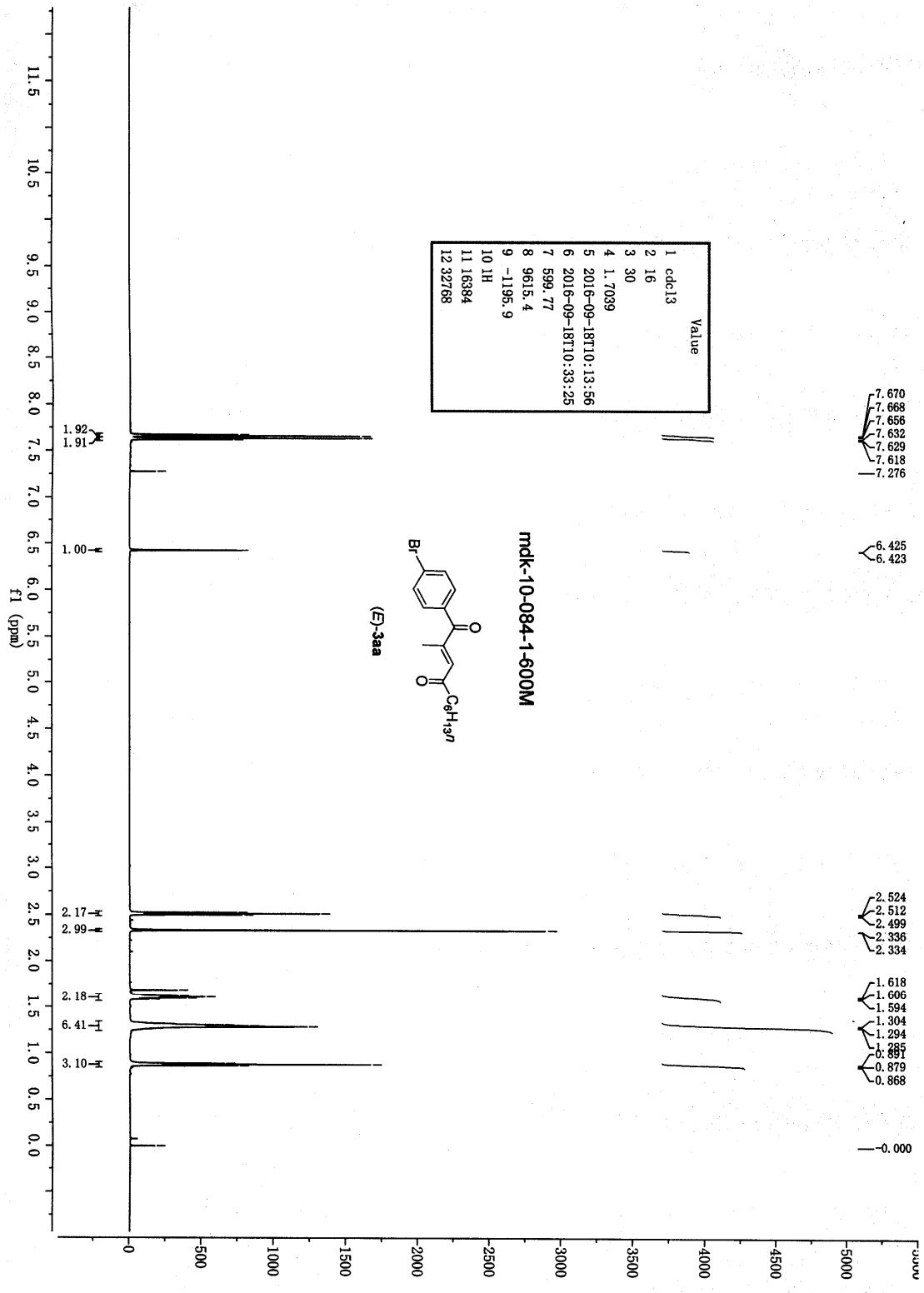

(E)-3ba
mdk-10-022-1-noe 2 1 C:\TOPSPIN\Bruker
F2 [ppm]
F1 [ppm]
8
6
4
2

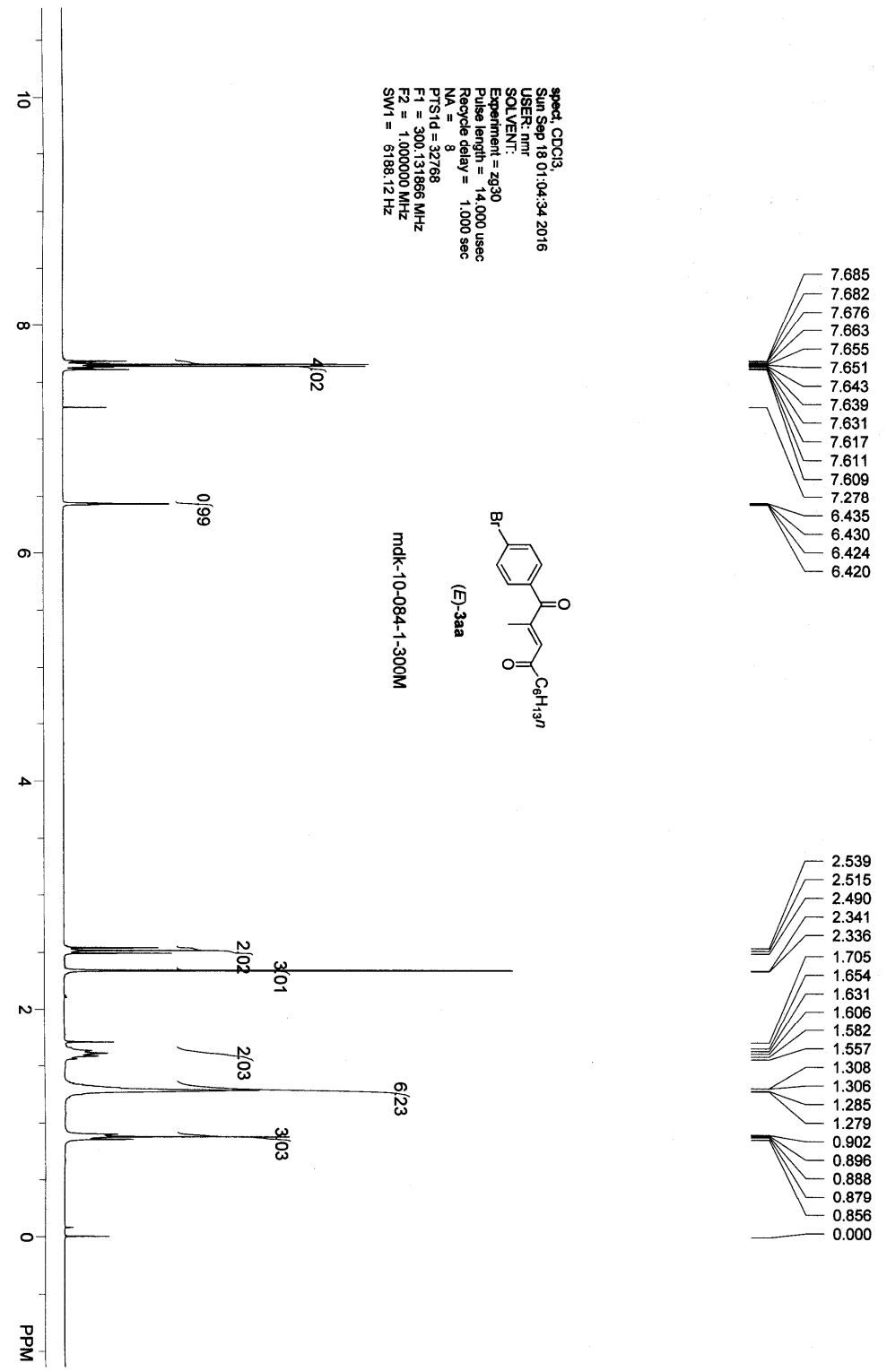

spect, CDCl3,
Tue Jun 07 08:25:11 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-10-022-2
(Z)-3ba
C8H13N
7.880
7.876
7.871
7.853
7.848
7.554
7.529
7.473
7.468
7.452
7.447
7.423
7.265
6.376
6.372
6.366
6.361
2.464
2.440
2.419
2.415
2.119
2.114
1.622
1.501
1.477
1.255
1.233
1.215
1.209
0.865
0.855
0.843
0.820
0.000
2.00
1.16
2.31
1.00
2.20
3.02
2.48
7.72
3.51
10
8
6
4
2
0
PPM

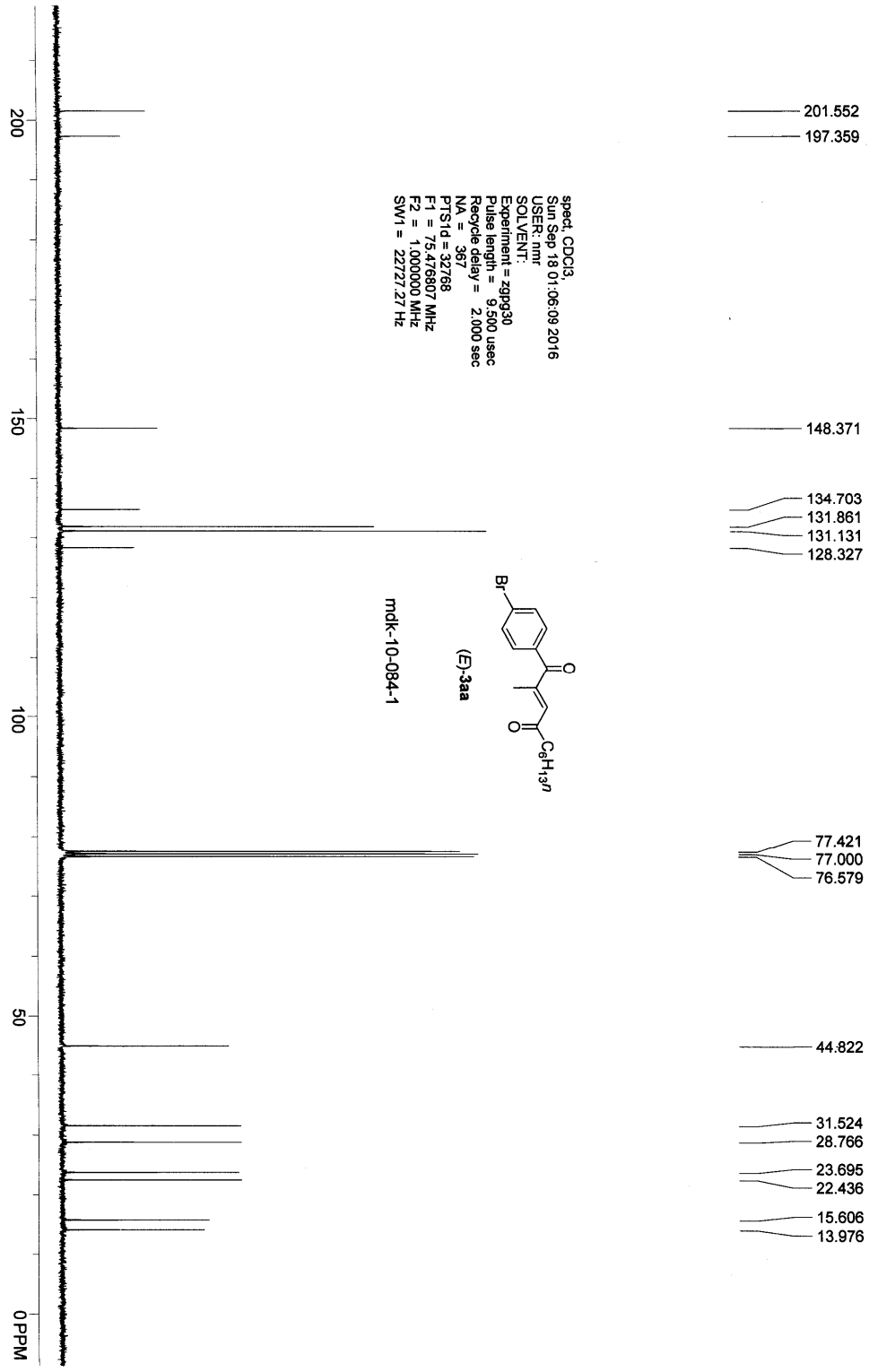

199.365
198.464
153.705
134.369
133.265
128.688
128.341
126.060
77.424
77.204
77.000
76.576
42.860
31.498
29.675
28.738
23.563
22.417
21.634
13.974
200
150
100
50
PPM
spect, CDCl3
Tue Jun 07 08:51:46 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 2238
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-10-022-2
(Z)-3ba
O
O
C8H13

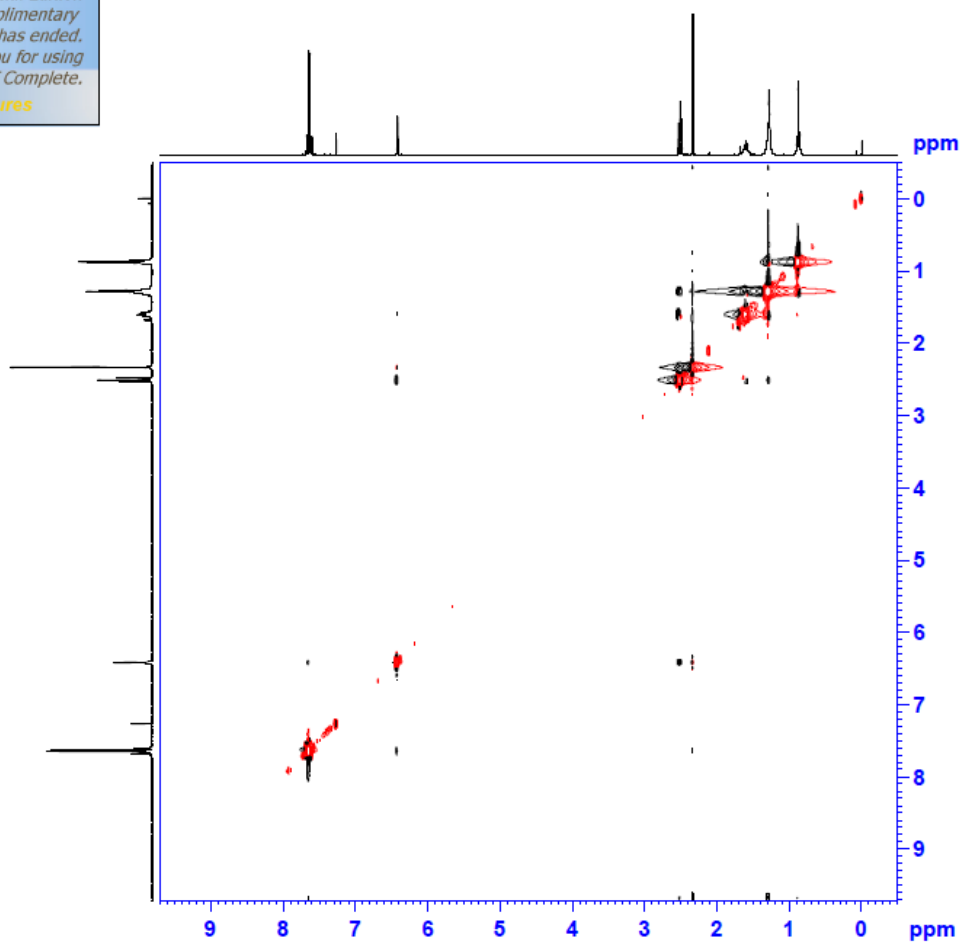

spect, CDCl3,
Wed Jun 08 01:10:39 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
7 uL CH2Br2 as internal standard
in 26.5 mg sample
mdk-10-022-2-purity
(Z)-3ba
40.84
100.00
7.877
7.852
7.848
7.554
7.473
7.447
6.373
6.368
4.930
2.465
2.440
2.416
2.119
2.114
1.661
1.256
1.214
1.209
0.865
0.843
0.820
-0.000
10
8
6
4
2
0
PPM

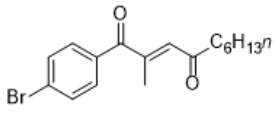

(Z)-3ba
O
O
C6H13n
mdk-10-022-2-noe 2 1 C:\TOPSPIN\Bruker
F2 [ppm]
F1 [ppm]
8
6
4
2


Value
1 cdcl3
2 16
3 30
4 1.7039
5 2016-09-18T10:13:56
6 2016-09-18T10:33:25
7 599.77
8 9615.4
9 -1195.9
10 1H
11 16384
12 32768
mdk-10-084-1-600M
(E)-3aa
Br
O
O
C6H13n
f1 (ppm)
1.92
1.91
1.00
2.17
2.99
2.18
6.41
3.10
7.670
7.668
7.656
7.632
7.629
7.618
7.276
6.425
6.423
2.524
2.512
2.499
2.336
2.334
1.618
1.606
1.594
1.304
1.294
1.285
0.891
0.879
0.868
0.000


spect_CDCl3_
Sun Sep 18 01:04:34 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-10-084-1-300M
(E)-3aa
Br
O
O
C6H13n
7.685
7.682
7.676
7.663
7.655
7.651
7.643
7.639
7.631
7.617
7.611
7.609
7.278
6.435
6.430
6.424
6.420
2.539
2.515
2.490
2.341
2.336
1.705
1.654
1.631
1.606
1.582
1.557
1.308
1.306
1.285
1.279
0.902
0.896
0.888
0.879
0.856
0.000
4.02
0.99
2.02
3.01
2.03
6.23
3.03
10
8
6
4
2
0
PPM

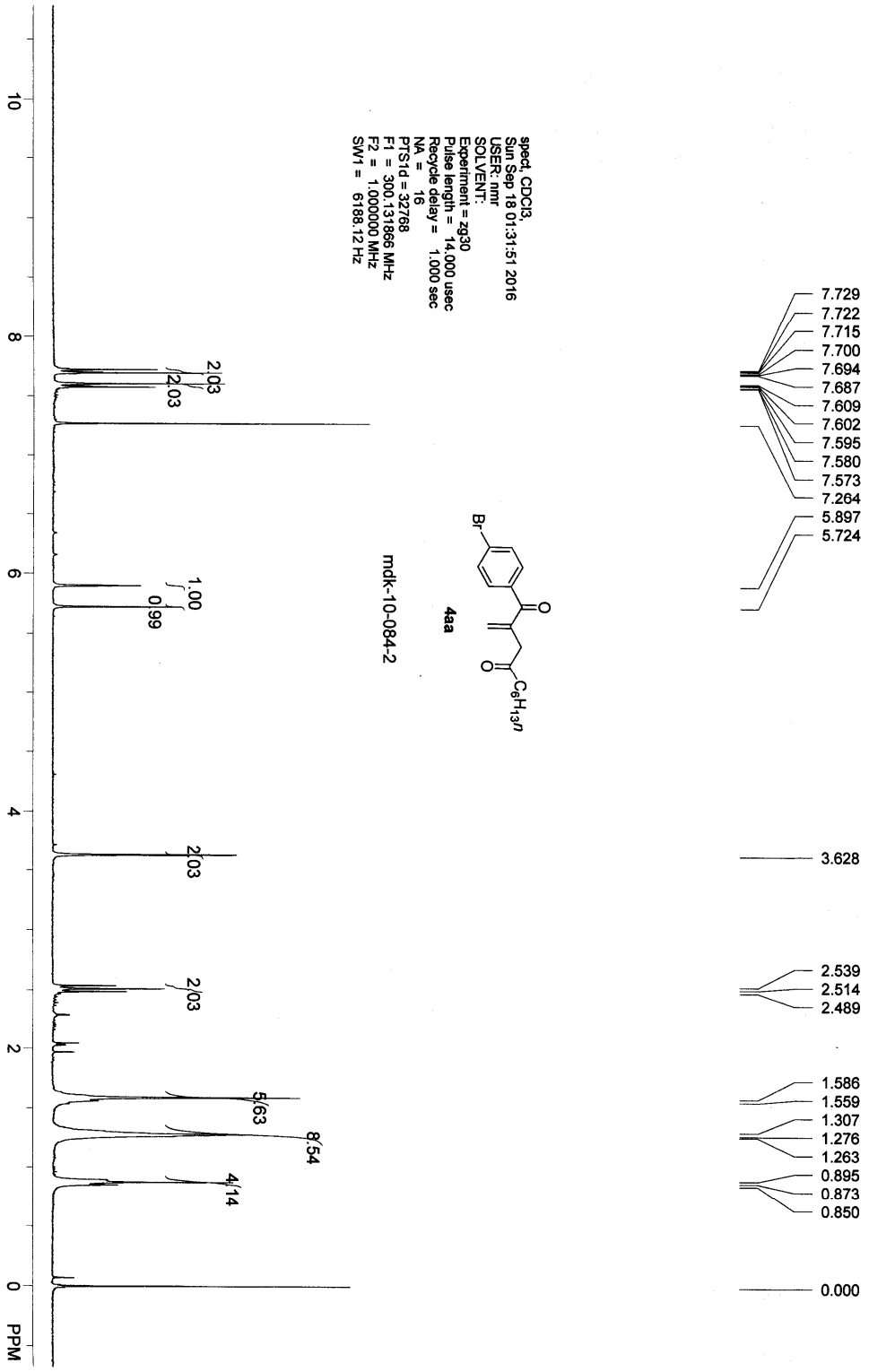

spect, CDCl3,
Sun Sep 18 01:06:09 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 367
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-10-084-1
(E)-3aa
Br
O
O
C8H13N
201.552
197.359
148.371
134.703
131.861
131.131
128.327
77.421
77.000
76.579
44.822
31.524
28.766
23.695
22.436
15.606
13.976
200
150
100
50
0 PPM

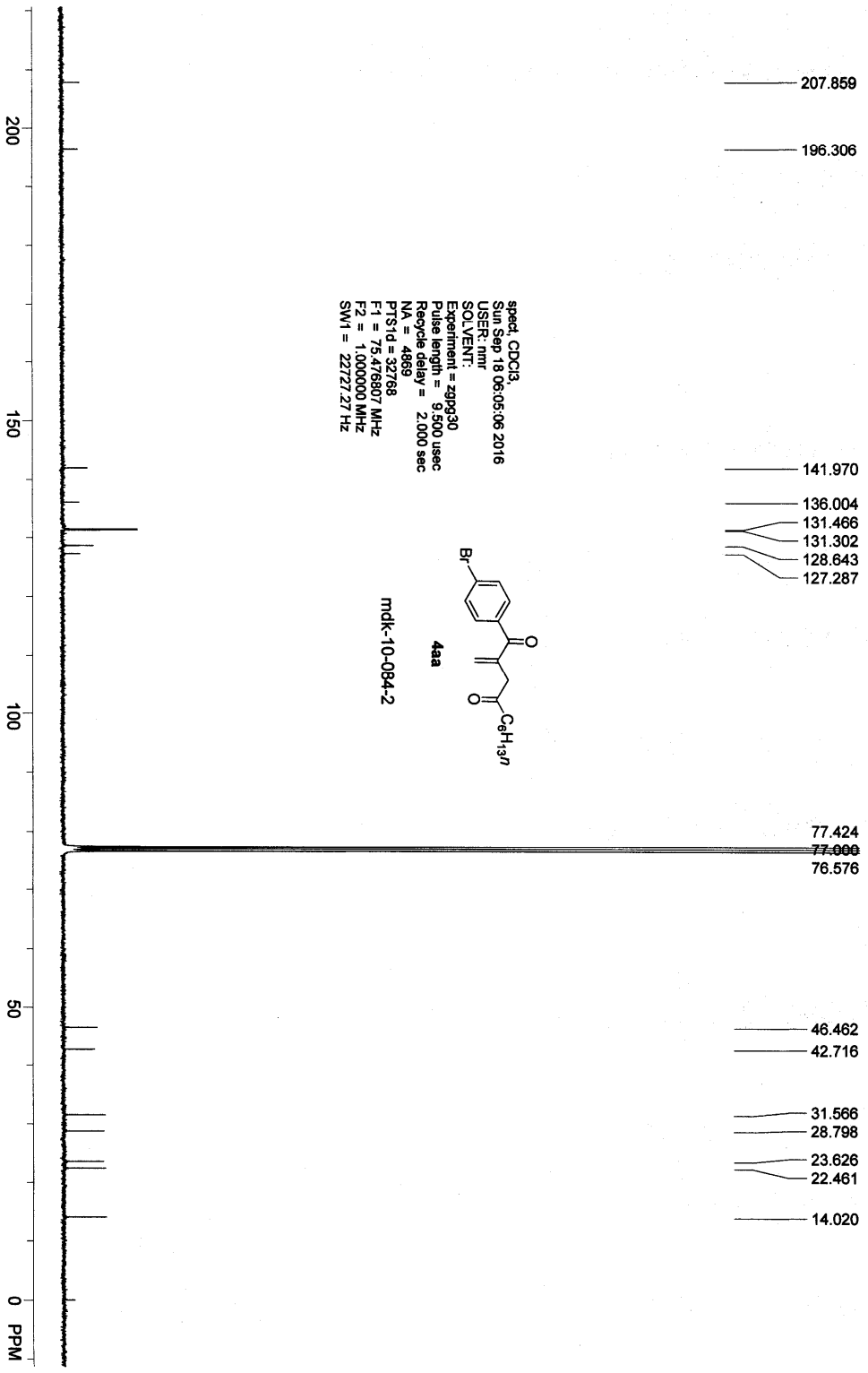


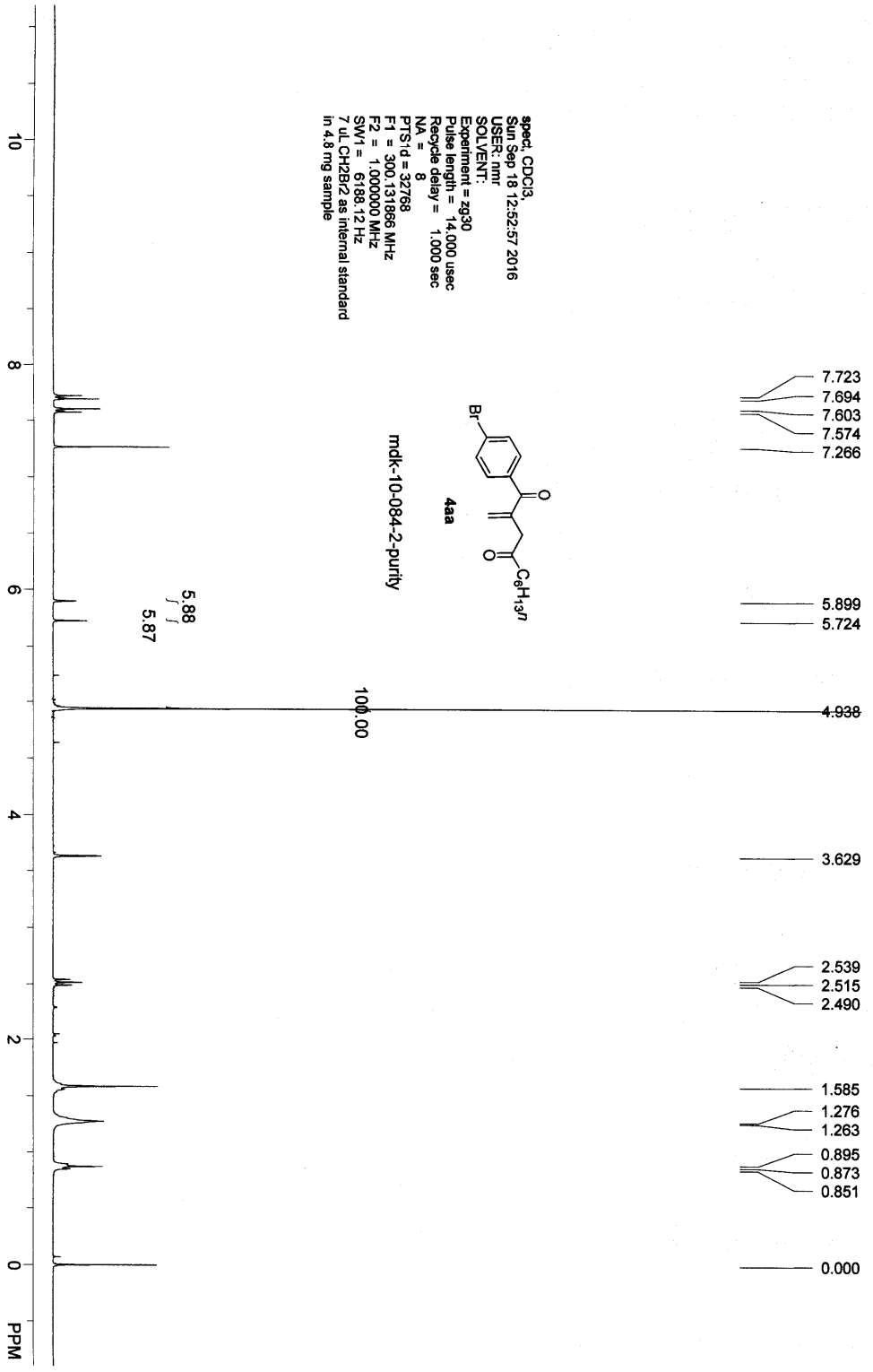


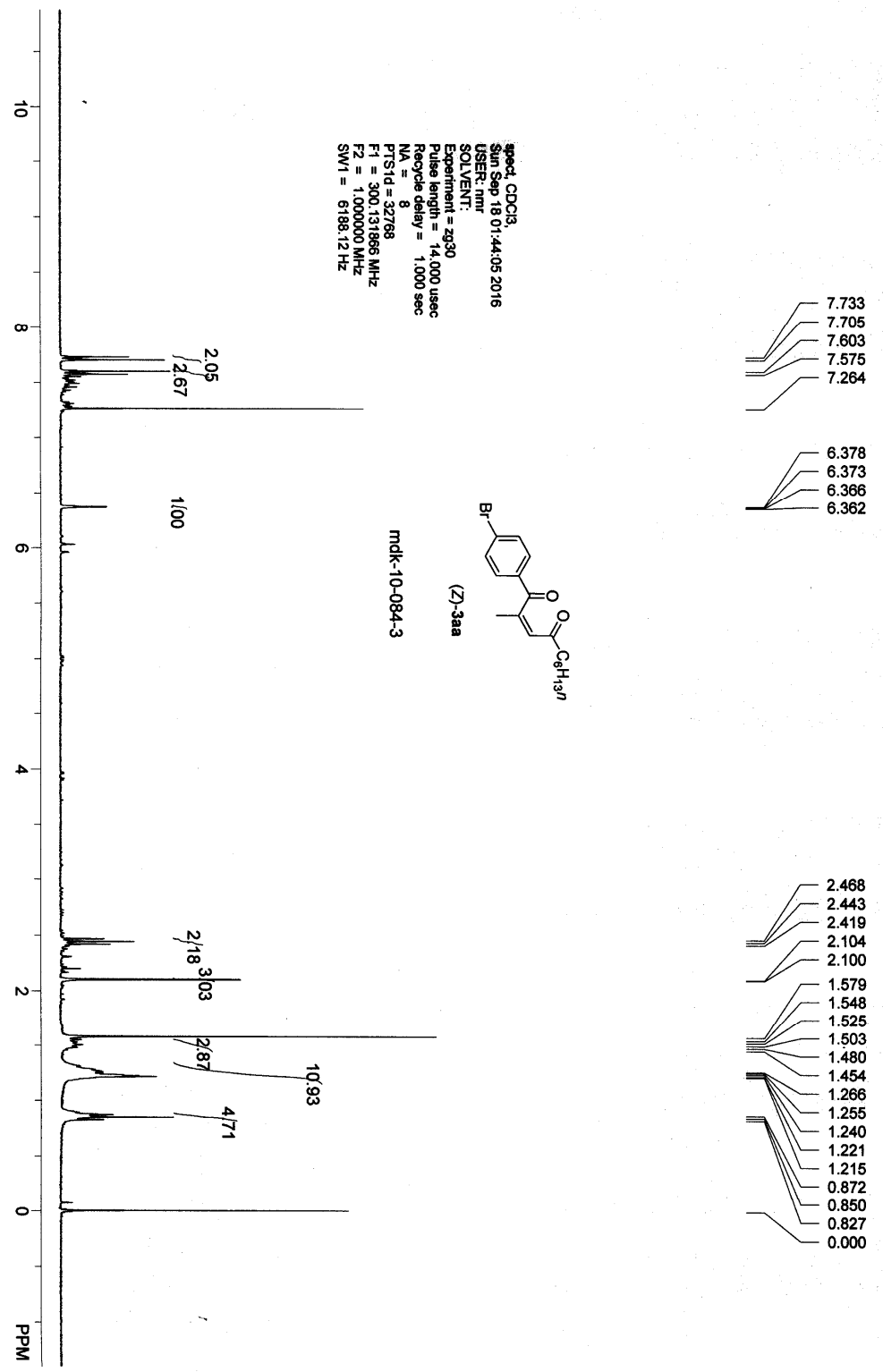
(*E*)-**3aa**

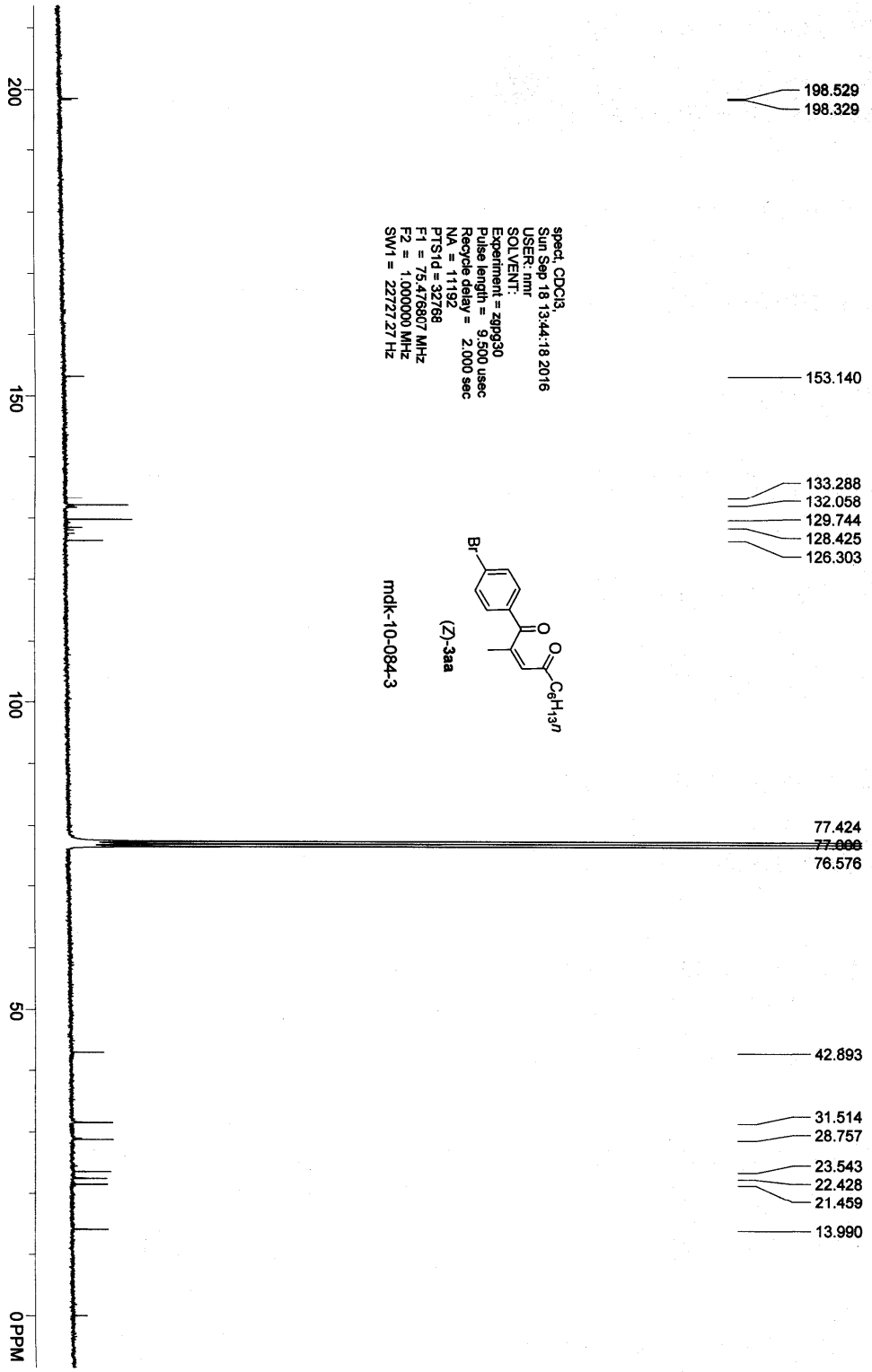
mdk-10-084-1-noe

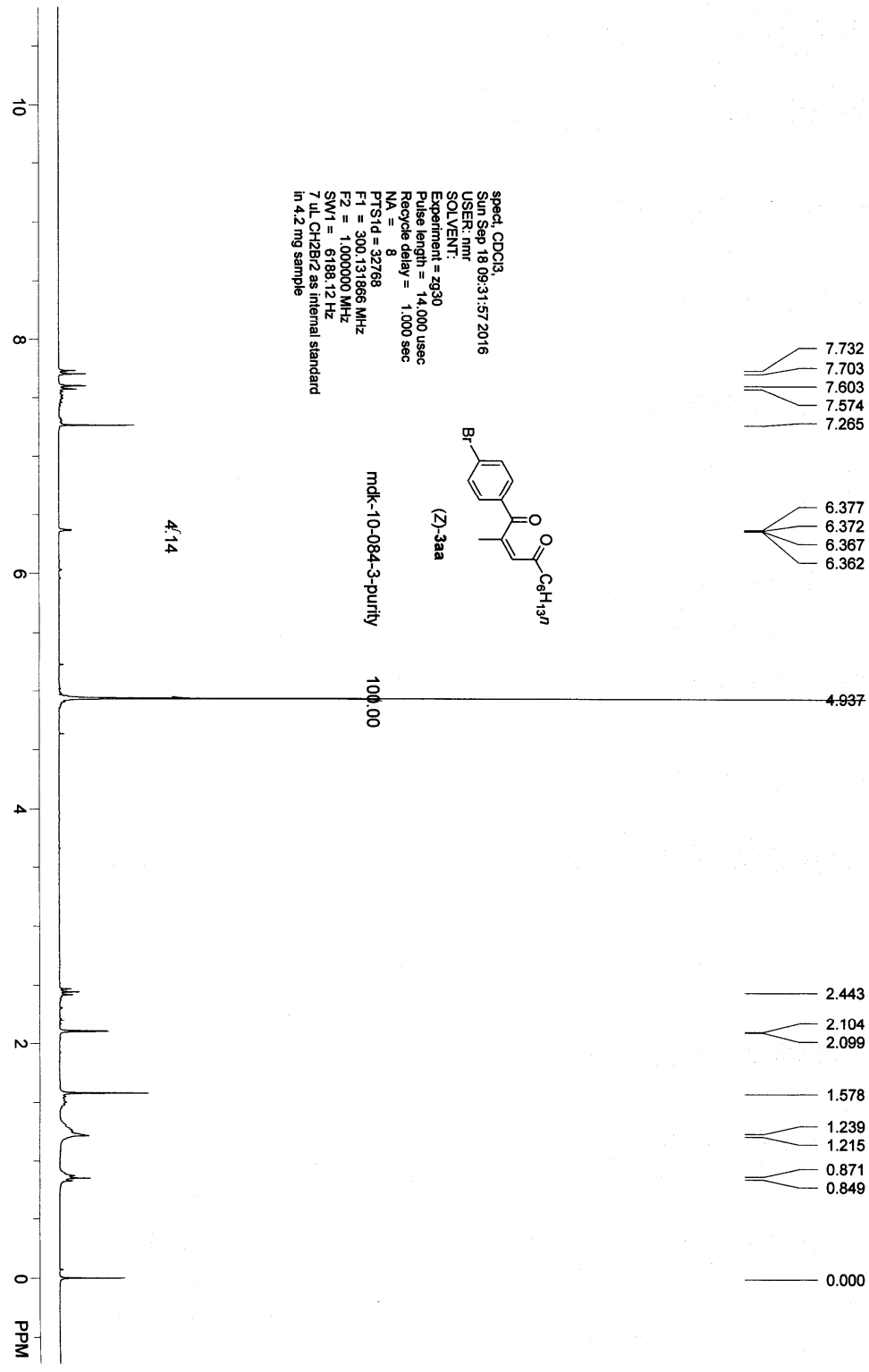

spect, CDCl3,
Sun Sep 18 01:31:51 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 16
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-10-084-2
4aa
Br
O
O
C6H13n
7.729
7.722
7.715
7.700
7.694
7.687
7.609
7.602
7.595
7.580
7.573
7.264
5.897
5.724
3.628
2.539
2.514
2.489
1.586
1.559
1.307
1.276
1.263
0.895
0.873
0.850
0.000
2.03
2.03
1.00
0.99
2.03
2.03
5.63
8.54
4.14
10
8
6
4
2
0
PPM

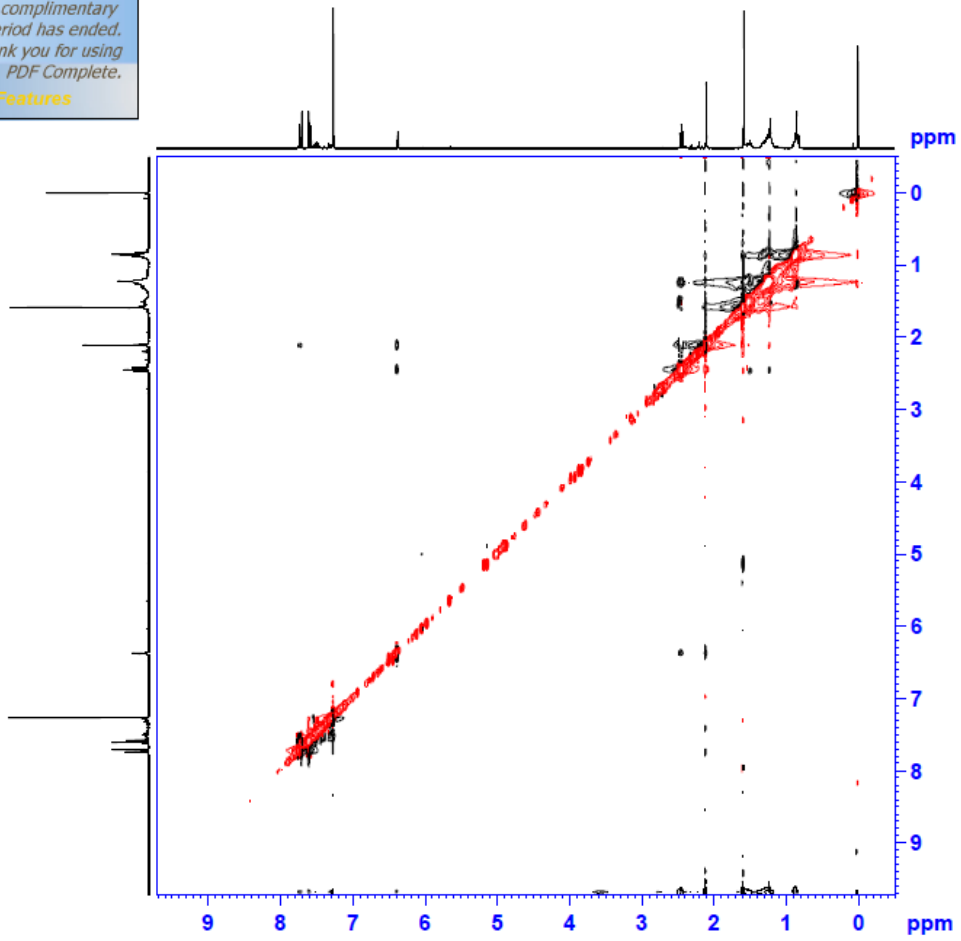

207.859
196.306
141.970
136.004
131.466
131.302
128.643
127.287
77.424
77.000
76.576
46.462
42.716
31.566
28.798
23.626
22.461
14.020
200
150
100
50
0 PPM
spect, CDCl3
Sun Sep 18 06:05:06 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 4869
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-10-084-2
4aa
Br
O
O
C6H13

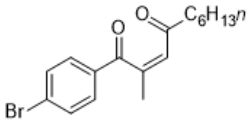

spect, CDCl3,
Sun Sep 18 12:52:57 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
7 uL CH2Br2 as internal standard
in 4.8 mg sample
mdk-10-084-2-purity
4aa
Br
O
O
C6H13n
7.723
7.694
7.603
7.574
7.266
5.899
5.724
4.938
3.629
2.539
2.515
2.490
1.585
1.276
1.263
0.895
0.873
0.851
0.000
5.88
5.87
100.00
10
8
6
4
2
0
PPM


spect, CDCl3,
Sun Sep 18 01:44:05 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-10-084-3
(Z)-3aa
Br
O
O
C6H13n
7.733
7.705
7.603
7.575
7.264
6.378
6.373
6.366
6.362
2.468
2.443
2.419
2.104
2.100
1.579
1.548
1.525
1.503
1.480
1.454
1.266
1.255
1.240
1.221
1.215
0.872
0.850
0.827
0.000
2.05
2.67
1.00
2.18
3.03
2.87
10.93
4.71
10
8
6
4
2
0
PPM


198.529
198.329
153.140
133.288
132.058
129.744
128.425
126.303
77.424
77.000
76.576
42.893
31.514
28.757
23.543
22.428
21.459
13.990
spect, CDCl3,
Sun Sep 18 13:44:18 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 11192
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-10-084-3
(Z)-3aa
Br
O
O
C8H17
200
150
100
50
0 PPM

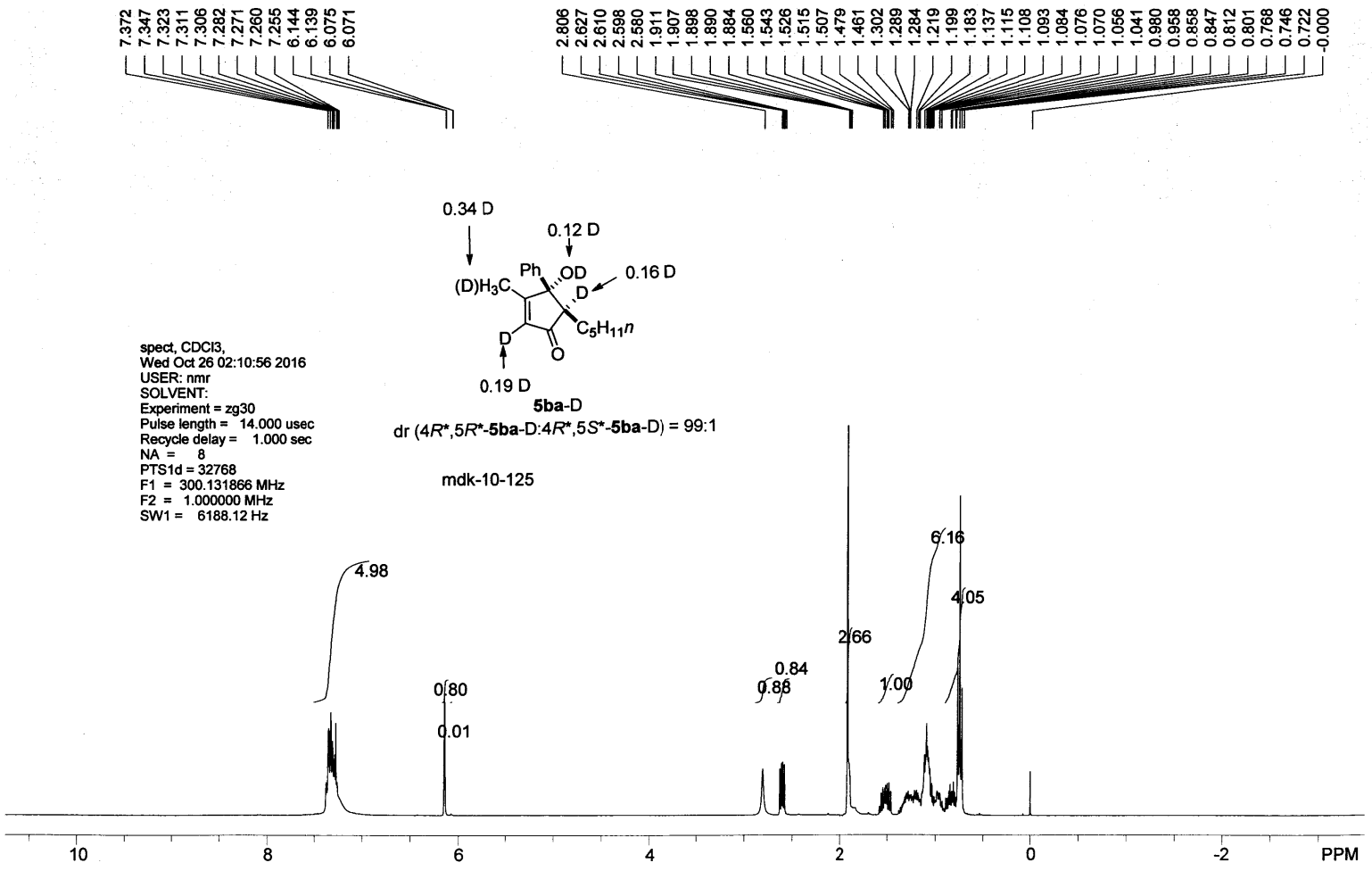

spect. CDCl3.
Sun Sep 18 09:31:57 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
7 uL CH2Br2 as internal standard
in 4.2 mg sample
4.14
mdk-10-084-3-purity
100.00
(Z)-3aa
Br
O
O
C6H13n
7.732
7.703
7.603
7.574
7.265
6.377
6.372
6.367
6.362
4.937
2.443
2.104
2.099
1.578
1.239
1.215
0.871
0.849
0.000
10
8
6
4
2
0
PPM

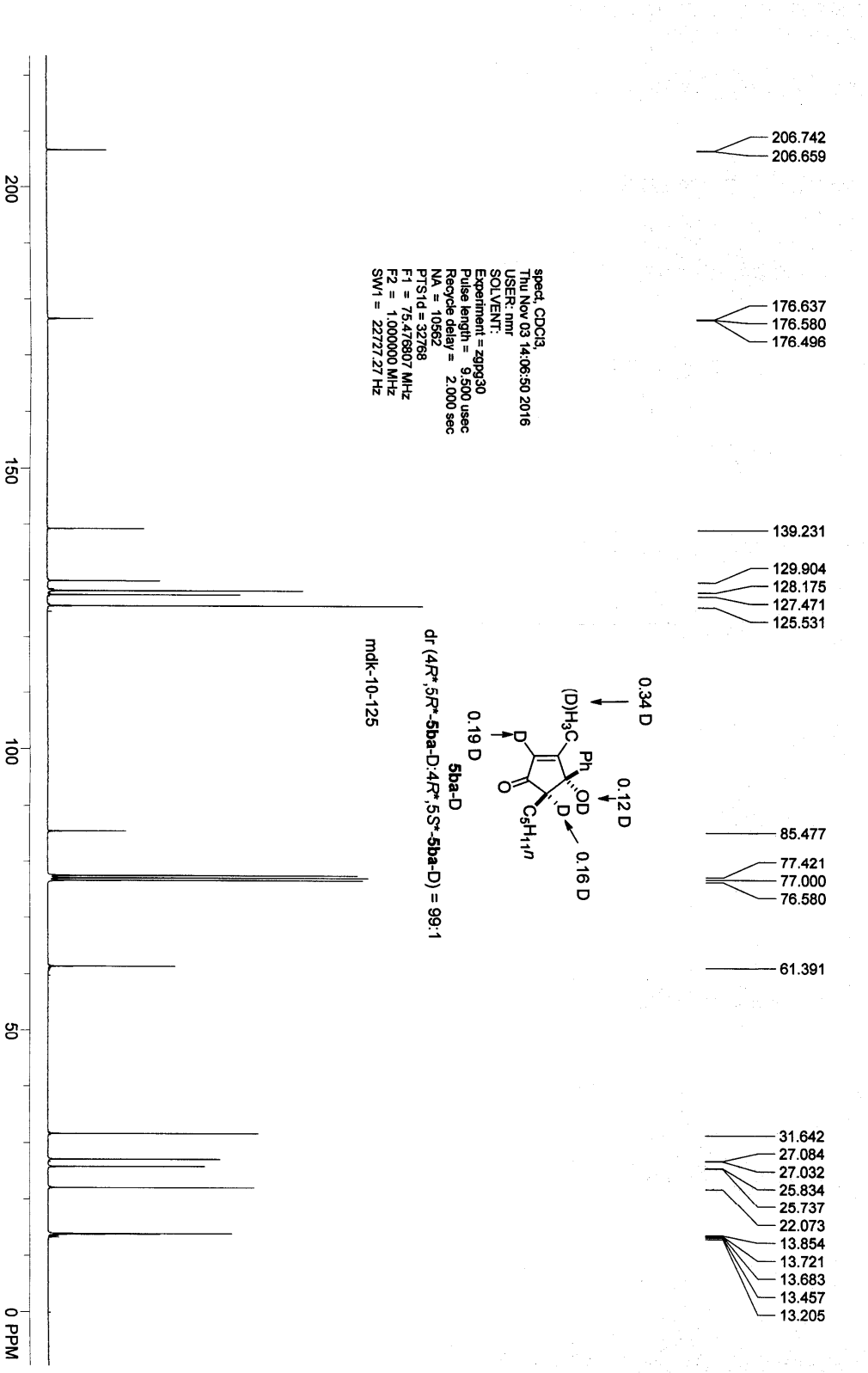




(Z)-**3aa**

mdk-10-084-3-noe


7.372
7.347
7.323
7.311
7.306
7.282
7.271
7.260
7.255
6.144
6.139
6.075
6.071
2.806
2.627
2.610
2.598
2.580
1.911
1.907
1.898
1.890
1.884
1.560
1.543
1.526
1.515
1.507
1.479
1.461
1.302
1.289
1.284
1.219
1.199
1.183
1.137
1.115
1.108
1.093
1.084
1.076
1.070
1.056
1.041
0.980
0.958
0.858
0.847
0.812
0.801
0.768
0.746
0.722
-0.000
0.34 D
0.12 D
0.16 D
0.19 D
Ph
OD
D
(D)H3C
C5H11n
O
5ba-D
dr (4R*,5R*-5ba-D:4R*,5S*-5ba-D) = 99:1
spect, CDCl3,
Wed Oct 26 02:10:56 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-10-125
4.98
0.80
0.01
0.84
0.88
2.66
1.00
6.16
4.05
10
8
6
4
2
0
-2
PPM


206.742
206.659
176.637
176.580
176.496
139.231
129.904
128.175
127.471
125.531
85.477
77.421
77.000
76.580
61.391
31.642
27.084
27.032
25.834
25.737
22.073
13.854
13.721
13.683
13.457
13.205
200
150
100
50
0 PPM
spect, CDCl3,
Thu Nov 03 14:06:50 2016
USER: mm
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 10562
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-10-125
dr (4R*,5R*-5ba-D:4R*,5S*-5ba-D) = 99:1
5ba-D
0.19 D
0.34 D
0.12 D
0.16 D
(D)H3C
Ph
OD
D
D
O
C5H11n